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ECHNOLOGY TRANSFER CONFERENCE

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PROCEEDINGS

VOLUME II
LIQUID & SOLID WASTE
ANALYTICAL METHODS
ENVIRONMENTAL SOCIO-ECONOMICS

A Decade of Sharing Results

November 20 & 21, 1989
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Introduction

Environment Ontario holds its annual Technology Transfer Conference to report and publicize the progress made on Ministry-funded projects. These studies are carried out in Ontario Universities and by private research organizations and companies.

The papers presented at the Environmental Research: 1989 Technology Transfer Conference are published in two volumes of conference Proceedings corresponding to the following sessions:

VOLUME I: FEATURE PRESENTATIONS
AIR QUALITY RESEARCH
WATER QUALITY RESEARCH

VOLUME II: LIQUID & SOLID WASTE RESEARCH
ANALYTICAL METHODS
ENVIRONMENTAL SOCIO-ECONOMICS

Volume II is comprised of presentations given during Session C, Session D and Session E of the conference.

For references purposes, indices for all sessions may be found at the front of both volumes.

For further information on any of the papers, please contact either the authors or the Research and Technology Branch at (416) 323-4574 or 323-4573.

Acknowledgments

The Conference Committee would like to thank the authors for their valuable contributions to environmental research in Ontario.

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SESSION C

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C2

THE MOBILITY AND PERSISTENCE OF SELECTED ORGANIC SOLUTES IN ANAEROBIC GROUNDWATERS AND POSSIBLE IN SITU REMEDIATION MEASURES

D. W. Acton, J. F. Barker, M. A. Shaw, F. Beaudet, J. A. Cherry
Waterloo Centre for Groundwater Research
University of Waterloo
Waterloo, Ontario N2L 3G1

ABSTRACT

The distribution of selected organic compounds in landfill leachate impacted groundwaters provides some evidence for natural attenuation of some contaminants. Biodegradation, even after a long acclimatization period, may be partially responsible for this passive remediation. Where active remediation is required, in situ biorestoration may be considered.

Our research has concentrated on the remediation of landfill contaminated groundwaters by the stimulation, in situ, of the anaerobic degradation processes of denitrification and sulphate reduction. Target organics include simple halocarbons and aromatic hydrocarbons, identified in previous studies as common landfill-derived groundwater contaminants. A series of laboratory and controlled field tests has indicate some organic contaminants are susceptible to biodegradation under these conditions. Field evaluations at both the North Bay landfill site and the CFB Borden site are continuing.

INTRODUCTION

Groundwater impacted by leachate from landfill sites is a serious environmental concern, especially when such groundwater is near drinking water wells or discharges into surface water bodies. Much of this concern has centred upon organic contaminants. We have found such leachates to contain reasonably mobile organic contaminants such as benzene, ethylbenzene, chlorobenzenes, chloroform, trichloroethylene, and similar compounds, albeit only at trace concentrations (< 100 ug/L) usually (Barker et al., 1988). Our research continues to focus upon these aromatic hydrocarbons and halocarbons.

Remediating groundwater contaminated by leachates typically involves collection of the contaminated groundwater and treating it. For sites removed from municipal wastewater treatment facilities, on site facilities can be established, but costs and uncertain performance limit this option. It is within the context of developing innovative technologies that we have been conducting research into the in situ biorestoration of landfill leachate impacted groundwaters.

In situ biorestoration is the stimulation of microbiological processes within the contaminated aquifer to cause the biodegradation of contaminants. This technology has been used with some success to clean up aquifers contaminated by petroleum hydrocarbons and shows promise for dealing with some halocarbon and other organic contaminants (Wilson et al., 1986). The approach is to identify what chemical additions to contaminated groundwater can stimulate the natural microbial community to biodegrade the contaminants. Then these favourable conditions must be created in situ. In many cases this treatment

approach resembles the wastewater treatment use of aerobic and anaerobic digestion. However, as it is done in situ considerable savings may be realized because large volumes of groundwater do not have to be removed from the aquifer.

Landfill leachates contain a broad range of inorganic and organic contaminants and so present a complex challenge for in situ biorestoration. Our research has concentrated upon aromatic hydrocarbons and simple halocarbons. If encouraging results are obtained, the fate of the numerous other contaminants in leachates will have to be evaluated before the technique can be recommended. Given the complex mixture of contaminants, in situ biorestroation will probably become only part of the treatment train for contaminated groundwaters.

Current aerobic techniques may be difficult to apply to anaerobic leachate contaminated groundwaters. For example, oxidation of iron and rapid biomass growth can product plugging of injection wells making further additions difficult. Therefore, we decided to evaluate anaerobic biodegradation of organic contaminants. Our approach has been to stimulate denitrifying, sulphate-reducing and anaerobic fermentative bacteria through simple chemical additions of the appropriate electron acceptors (nitrate, sulphate, and organics, respectively). This approach, if successful, will be technically simple and economically attractive.

Biodegradation occurs in leachate plumes naturally. Our research is continuing to evaluate natural biodegradation of organic contaminants in some landfill leachate plumes. In some situations, the natural dispersive dilution and biodegradation processes may be sufficient to protect the environment and no positive intervention may be warranted. This "passive remediation" option will require an excellent scientific basis before regulatory agencies can accept it.

These studies have involved laboratory experiments, in which aquifer conditions and remediations are represented in a well-controlled setting, and field experiments, where actual aquifers are encountered. This research project will not be completed until 1990, so only some aspects are presented here.

NATURAL BIODEGRADATION IN AN EXISTING LEACHATE PLUME

Monitoring of groundwater quality at the New Borden landfill site, CFB Borden, near Barrie, has continued from 1985 to the present. Sampling has concentrated upon the initial cell (60m x 150m) which received municipal refuse from 1976 to 1979. A plume of contaminated groundwater emanates from the cell and extends about 150m north in sandy and silty tills. Figure 1 shows the monitoring well locations. At each site, two or three piezometers were installed. Figure 2 shows the distribution of the maximum benzene concentrations found at each site during July/August 1985, 1987, 1988 and 1989. Sampling in 1985 was not comprehensive. Whereas low concentrations of benzene were found well to the north of the cell in 1987, detectable benzene became sporadic here in 1988 and was not detected (< 1.1 ug/L) in 1989. Concentrations remained above 10 ug/L in and adjacent to the cell over this period, without a trend to lower leachate concentrations (B84-2 and B84-3 are within the waste). Thus, the general decline in trace benzene concentrations in the plume may be attributed to increasing attenuation over time, rather than to declining source or input concentration. Such a trend is at least consistent with an increase in benzene biodegradation over time. This could represent a long acclimatization period (8 to 13 years) before the onset of slow anaerobic benzene biodegradation. A more

comprehensive review of other solute data is underway to see if the benzene behaviour is anomalous. It appears that halocarbons such as chloroform, trichloroethylene and trichloroethane have suffered large concentration declines even within the leachate from 1985 to 1989. These could reflect a decline in these chemicals in the leachate source or they could reflect more complete biodegradation under the methanogenic conditions developing within the waste. In any case, the natural attenuation of these trace organics at this site is impressive.

IN SITU BIORESTORATION

Borden Experimental Aquifer

An anaerobic, landfill leachate plume emanates from the abandoned landfill site at CFB Borden. It was found to be essentially free of aromatic hydrocarbons and halocarbons, typically found in other landfill leachate plumes (Barker, 1987). A segment of this aquifer has been and is being used for a number of field experiments evaluating the migration and fate of aromatic hydrocarbons and halocarbons (Mackay et al., 1985; Barker et al., 1987). Recently, with the support of the Petroleum Association for Conservation of the Canadian Environment (PACE), the possible remediation of gasoline contaminated groundwater through the in situ stimulation of denitrifying bacteria has been evaluated. As part of the MOE-supported remedial research, we are currently also evaluating the fate of aromatic hydrocarbons following the stimulation of sulphate reducing bacteria. This contaminated aquifer already contains about 150 mg/L SO4. Sulphate reduction appears to be limited by the lack of organic substrates, rather than by the lack of sulphate. In both laboratory and small-scale field column tests, we have been able to stimulate sulphate reducing bacteria by the addition of organic substrates such as lactate, acetate and yeast extract. To date, laboratory experiments have not found aromatic hydrocarbon biodegradation under sulphate reducing conditions. These experiments are ongoing. Laboratory and field column evaluations of halocarbon fate under induced sulphate reduction have also been initiated.

North Bay Aquifer

The leachate contaminated groundwater at the North Bay landfill site contains up to 100 ug/L of various aromatic hydrocarbons and less than 10 ug/L of halocarbons (Barker, 1987). Much of the contaminated aquifer is methanogenic and the aromatics, at least, appear to be somewhat persistent (Barker and Mayfield, 1988). Most of our anaerobic in situ biorestoration research has focused upon this site.

Initial laboratory experiments, using North Bay aquifer sand and groundwater ammended with additional organic contaminants and remedial additions indicated some promise for degradation of such compounds as carbon tetrachloride, trichloroethane, xylenes and ethylbenzene. Field column experiments also produced evidence of similar degradations. In these experiments, in situ columns of about 1 litre pore volume are flushed with groundwater spiked with up to 200 ug/L of similar organics and with sulphate or nitrate remedial additions and then sampled periodically. Eventually, native groundwater re-enters the column as samples are withdrawn, thus ending the experiment. Acton and Barker (in prep.) describe the procedure. The columns are described by Gillham et al. (in sub.).

Figure 3 shows the changing concentrations of bromide, the conservative tracer, remedial additions (nitrate and sulphate), carbon dioxide generated, nitrous oxide and methane concentrations and selected organics during the 105 day field column experiments. The reasonably constant bromide values indicated that the spiked water introduced into the column did not undergo significant dilution by native groundwater and so other solute concentration changes likely represent the result of reactions within the aquifer included within the column. Nitrate was consumed and nitrous oxide was produced in another column to which an acetylene block was also added, demonstrating that denitrification did occur in column N. Not much sulphate reduction or methane production is evident in column S.

Under denitrifying conditions, few aromatics were removed. With sulphate addition and perhaps very minor sulphate reduction, impressive losses of aromatics was noted (Figure 3).

Many of these experiments were repeated this summer and the results are being evaluated. Interestingly, in all anaerobic field or lab experiments, rapid loss of carbon tetrachloride with some appearance of chloroform was found. This is consistent with a reductive dechlorination of carbon tetrachloride with 10 to 25% converted to chloroform, which then slowly decreased over the 200 day tests. Although the reaction may be microbially-mediated, the fact that it occurred under a variety of reducing conditions suggests that it is abiotic.

Sulphate reducing conditions appeared to stimulate a variety of aromatic and halocarbon degradations and so a field test of its efficacy has begun. At an experimental site within the North Bay plume, contaminated groundwater is withdrawn, spiked with bromide tracer, selected contaminants (benzene, toluene, ethylbenzene, xylenes and 1,2,4-trimethylbenzene) and sulphate remedial solution, and reinjected below the water table into the contaminated aquifer (see Figure 4). This injection will continue as long as possible this fall, with monitoring of the progress and fate of the organics within 10m of the injection wells using a detailed multilevel sampling well network.

FURTHER RESEARCH NEEDS

Such experiments address the microbiological aspects of anaerobic in situ remediation, but do not address the important aspects of how a remedial solution can be mixed, in situ, with the dissolved contaminants. Berry-Spark and Barker (1987) demonstrated that the natural processes of advection, dispersion and retardation produced such a mixing in the Borden aquifer, but such mixing will depend on site specific hydrogeological conditions. Some sites may not permit sufficient addition of remedial solutions or may not permit sufficient mixing. These and other, mainly microbiological, limitations will mean that in situ biorestoration will not be the panacea for the clean up of groundwater contaminated by organics. This research has begun the evaluation of the place of this novel remedial technology within the options for restoring contaminated groundwaters.

Nor does the current research adequately identify the impact of the in situ remedial measures on other water quality parameters. In the current field test at North Bay some attention will be paid to inorganic parameters such as reduced nitrogen and metals and to organic parameters such as phenol and acids. However, at other sites different contaminants may be of concern and the current research will not be adequate to address such concerns. Clearly, a better understanding of anaerobic processes in groundwaters is

required in order to extrapolate our studies to other sites. As part of this generalization process, additional site studies will also be necessary.

No one remedial strategy will work for all contaminated groundwaters. As our appreciation of the potential of in situ biorestoration improves, there will be a need to consider it within the capabilities, strengths and weaknesses of other remedial technologies, particularly the pump and treat methods. Even now, it may be useful to direct research in biorestoration into those combinations of chemicals and site conditions not likely to be easily dealt with by other technologies. Unfortunately, all remedial methods seem to be best suited to permeable aquifers. However, in situ biorestoration may be best suited to biodegradable contaminants that are strongly sorbed and therefore difficult to remove by pumping.

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Figure 1. New Borden landfill site plan, showing landfill cells and location of monitoring wells sampled in this study.

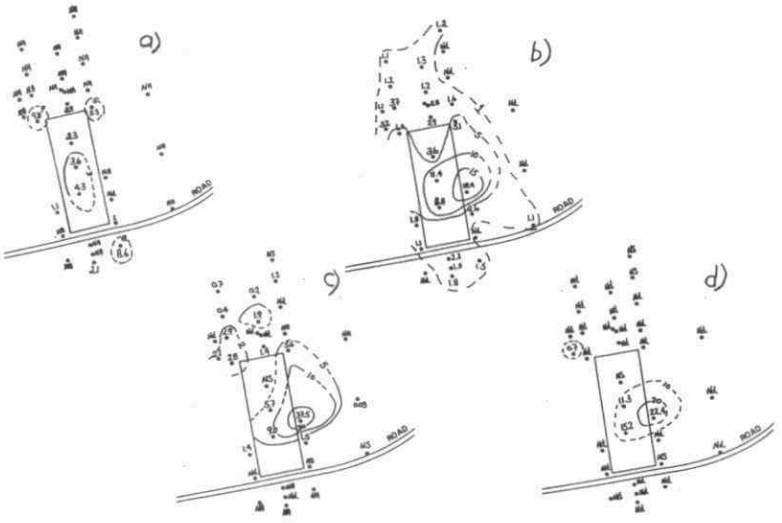


Figure 2. Contours of maximum benzene concentration in groundwater at each monitoring site for 1985 (a), 1987 (b), 1988 (c), 1989 (d). Benzene concentrations are in ug/L. NA - not analyzed; ND - below detection (about 1.1 ug/L); NS - not sampled.

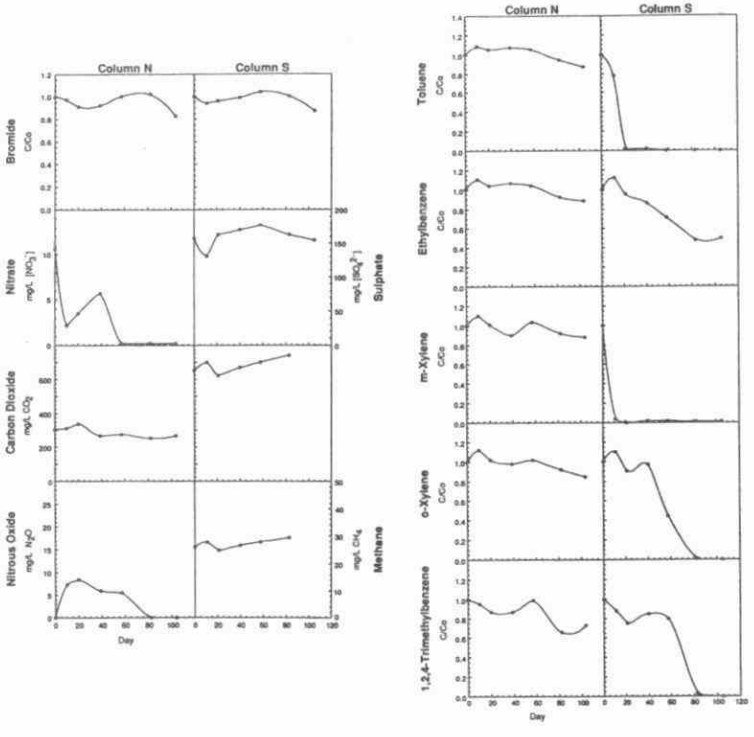


Figure 3. Relative concentrations in pore waters from column experiments in which stimulation of denitrifying (N) and sulphate reducing (S) conditions were attempted.

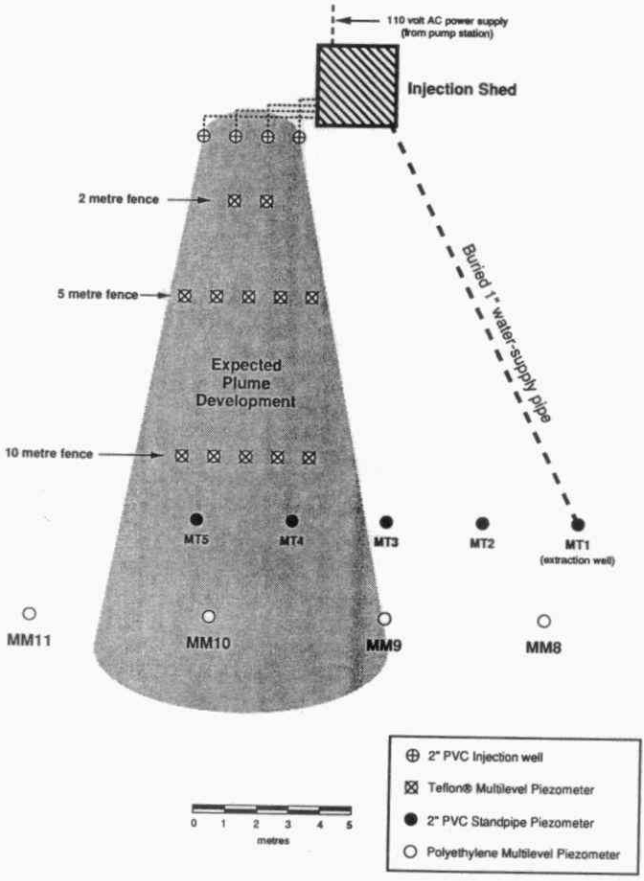


Figure 4. The plan view of the injection experiment at the North Bay site. Groundwater is obtained from well MT 1, spiked, injected and monitored over a 10m travel distance.

EXPERIMENTS WITH REMOVAL OF VOLATILE CONTAMINANTS FROM SOIL BY FORCED AIR VENTING

W.B. Benson, G.J. Farquhar, and E.A. McBean
Department of Civil Engineering
University of Waterloo
Waterloo, Ontario, N2L 3G1

1 Introduction

This paper presents some recent results from a research programme studying the behaviour of hazardous immiscible liquids and their vapours in soil. This program has been in progress since 1983 in the Department of Civil Engineering at the University of Waterloo. Part of this study is currently focussed on the practice of forced air venting as a means for removing volatile contaminants from soil, and it is this work to which this paper is addressed. Presented are results of laboratory venting experiments as well as a mathematical model used for simulating the experimental results. Initial experimentation for this project was described previously by Farquhar, et al., 1988.

2 Background

In recent years, soil venting has gained increased exposure as a remediation method for spills of volatile organic contaminants. Removal is achieved by enhanced advective vapour phase transport, induced by withdrawing or injecting air through wells screened in the unsaturated zone. Contaminant vapours are swept along the induced air flow path toward withdrawal wells, where they are removed and treated or released directly to the atmosphere. Constant recharging of the unsaturated zone with fresh air leads to increased contaminant volatilization. Several successful applications of soil venting for solvents and light hydrocarbons have been reported within the recent past, by Zimmermann and Brizgys, 1986; Hoag and Cliff, 1987; and Baehr, et al., 1989, to name a few. However, the predictability of the method is still very poor. Applications of soil venting as a remediation technique are performed

with little advance knowledge of how to design and operate an optimum system and without reliable estimates of the extent of clean up that is possible and the time in which it can be achieved.

Laboratory scale column experiments performed by others (Marley and Hoag, 1984, Baehr, et al., 1989, Johnson, et al., 1987) have tended to show that local liquid–vapour equilibrium exists in the porous medium, and the chemical concentrations in the exhaust vapour are at or near their saturation limits. If the chemical source is a multi–component mixture, such as gasoline, the resulting exhaust concentrations show a decline over time, due to selective volatilization of the more volatile components. In column experiments, this process has been simulated successfully (Baehr, et al., 1989) using an equilibrium based model to predict the vapour concentration of each component in the exhaust gas, based on the vapour pressures. A feature of these column experiments was that the entire cross–section of the column was at residual saturation with the hydrocarbon source. In large scale experiments (Wootan and Voynick, 1984, Rainwater, et al., 1988) and field applications, where the contaminant source is discontinuous, concentrations in the exhaust gas are significantly less than equilibrium saturation levels. It can be surmised that this is due to air flow through uncontaminated soil zones where no residual is present and in such cases there is no basis for predicting the chemical removal rate. Similarly, mathematical models formulated for the analysis of soil venting (Baehr, et al., 1989, Stephanatos, 1988) assume linear instantaneous equilibrium relationships for the description of interphase transfer between the liquid and aqueous phases and the gas phase.

2.1 Objectives

The purpose of this study can be summarized as follows:

1. to examine the validity of the equilibrium saturation assumption using laboratory column experiments

2. to devise experiments in which the chemical source would more closely simulate a contaminant spill and the resulting vapour concentrations from venting would be less than saturation levels

3. develop a predictive relationship to describe this behaviour based on experimental results and relevant theoretical considerations.

Table 1: Soil Properties

Intrinsic Permeability (k)	$1.45 \times 10^{-7}\ cm^2$
Porosity	0.4
Organic Content	0.17% dry wt.
Water Content	0.035% dry wt.
Bulk Density	$1.60\ g/cm^3$

3 Experimental Work

Laboratory experiments were conducted to observe and to quantify the rate at which a chemical source in a porous medium would volatilize and subsequently be transported under a forced air flow. Experiments were performed in vertical columns and in a large rectangular flux box. The principal variables were air flow rate, chemical type, and the size and shape of the contaminant zone to be removed.

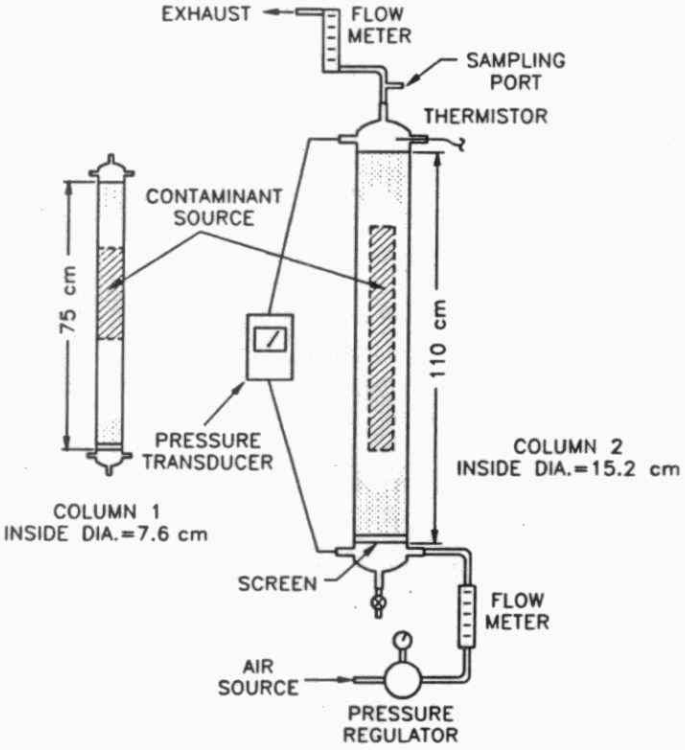
3.1 Materials and Equipment

Experimentation made use of two columns of different sizes, shown in Figure 1. Air flow was introduced into the column from the bottom using positive pressure. The desired flow rate for each experiment was set initially using the inlet flow meter, and outflow was monitored over the course of the experiment since it was a function of the chemical concentration in the exhaust gas. Vapour samples were drawn from the exhaust line, immediately after the gas exited from the column, and were analysed by gas chromatography.

A series of experiments were performed in a large box, illustrated in Figure 2. This box had been constructed for earlier work by Kell (1988) and was fitted with two vents to make it suitable for soil venting. Instrumentation for the box experiments was similar to that used for the columns. The design and operation of the experimental equipment is described in more detail elsewhere (Farquhar, et al., 1988, Benson, 1989).

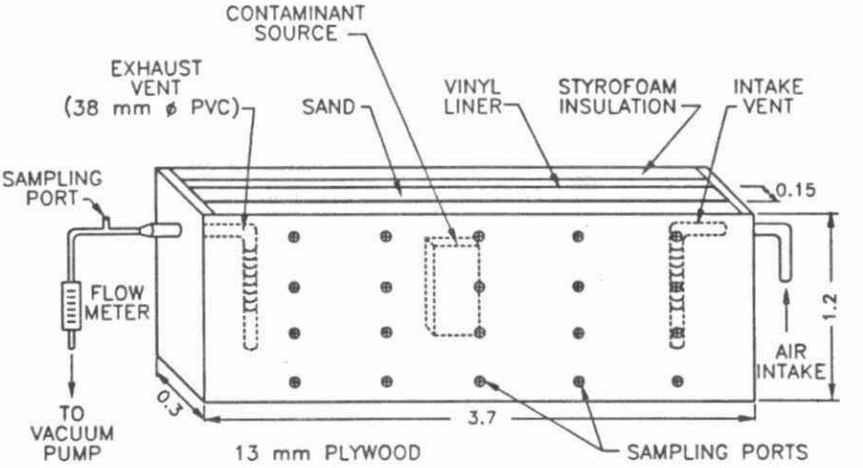
The soil used for all experiments was a fine, uniform Ottawa sand. Soil properties are listed in Table 1.

Three different chemicals were used in this study, hexane, heptane, and trichloroethylene (TCE), with hexane being used predominantly. All three



SOIL VENTING COLUMNS

Figure 1:



SOIL VENTING BOX

Figure 2:

Table 2: Chemical Properties

	Hexane	Heptane	TCE
Formula	C_6H_{14}	C_7H_{16}	C_2HCl_3
Vapour Pressure ($mmHg, 20°C$)	124	40	60
M.W. ($g/mole$)	86.2	100.2	131.4
Density (g/cm^3)	0.67	0.68	1.46

chemicals are considered volatile and are good candidates for removal from soil by venting. Chemical properties are summarized in Table 2.

3.2 Column Experiments

3.2.1 Column 1 : Chemical source occupying entire cross–section.

Initial experiments were carried out in the smaller of the two columns. In these experiments, the chemical was poured into the sand–packed column from the top and allowed to migrate downward, for a period of 4.5 hours. Separate experimentation showed that after 4.5 hours the chemical was at a residual saturation of 72 ml per litre of sand, which was approximately 60% of its ultimate residual saturation capacity. After 4.5 hours, the column was topped up with clean sand, capped and vented from the bottom with an air flow of 0.5 l/min, which translates to a specific discharge of 11.0 cm/min. Effluent vapour concentrations were monitored over the course of the run. This experiment was performed using three different chemicals, hexane, heptane, and TCE, with a constant volume (90 ml) added to the column for each run. The results presented in Figure 3 show that the exhaust concentration for hexane and heptane quickly reached its saturated equilibrium value and remained near this level over the course of the run before declining quickly to near zero. The exhaust concentrations of the denser TCE remained at approximately 85% of the saturation concentration.

Two variations of this experiment were also performed. In the first, sand was initially mixed with hexane and packed into the column at a residual content substantially less than the estimated ultimate residual saturation capacity. In the second variation, the sand packed column was initially satu-

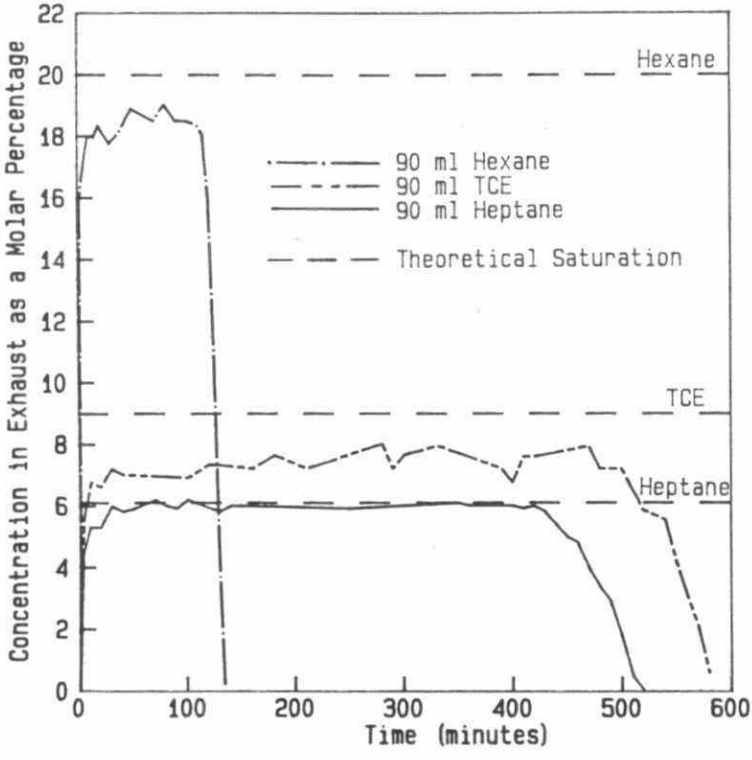


Figure 3: Chemical concentrations in exhaust gas with entire cross-section of column at residual saturation (inflow 0.5 l/min).

rated with water and allowed to drain to its field capacity before the hexane was added. In both cases, the resulting hexane concentration in the effluent gas was essentially unchanged from that presented in Figure 3.

3.2.2 Column 2 : Chemical source as a residual core in the soil.

A second set of experiments was performed in the larger column, using hexane exclusively as a chemical source. In order to draw conclusions regarding the effect of spill geometry on removal characteristics, it was necessary to introduce the chemical into the sand in such a way that the dimensions of the resulting contaminated zone would be known. This was accomplished by containing the hexane, as it migrated downward, within a form packed inside the column. This form could subsequently be removed to produce a cylindrical zone containing hexane at a known residual saturation.

Initial experiments were performed with the interior confining tube in place, in order to isolate the chemical removal due solely to air flowing through the zone of contamination. Air flow rates of 0.5, 1.0, 3.0, and 5.0 l/min were used. The corresponding specific discharges were 2.7, 5.5, 16.4, and 27.4 cm/min, respectively. These velocities are relatively high by field standards and would be most likely to occur in the vicinity of the discharge well. The results for a single experiment are shown in Figure 4. These results show both the exhaust hexane concentration (mg/l) and the mass removal rate of hexane (mg/min) over time, for various flow rates. It can be seen that the hexane concentration remains constant, independent of the air flow rate, and as a result the mass removal rate is solely a function of air flow rate. It can be concluded that the portion of the total air flow that passes through the interior column of residually saturated sand emerges saturated with hexane vapours and is therefore not affected by changes in the air velocity. The concentration in the exhaust gas is substantially less than saturation levels due to the diluting effect of the air that passes outside of the contaminant zone.

In subsequent experiments, the confining form was removed from the column, leaving a cylindrical plug of contaminated sand. This plug could have a diameter of either 4.8 cm or 7.5 cm, and its height was dependent on the volume of hexane. This volume ranged from 60 ml to 120 ml which, for a 4.8 cm diameter form, would result in heights ranging from 48 cm to 96 cm. As before, the air inflow varied from 0.5 to 5.0 l/min. Results from four

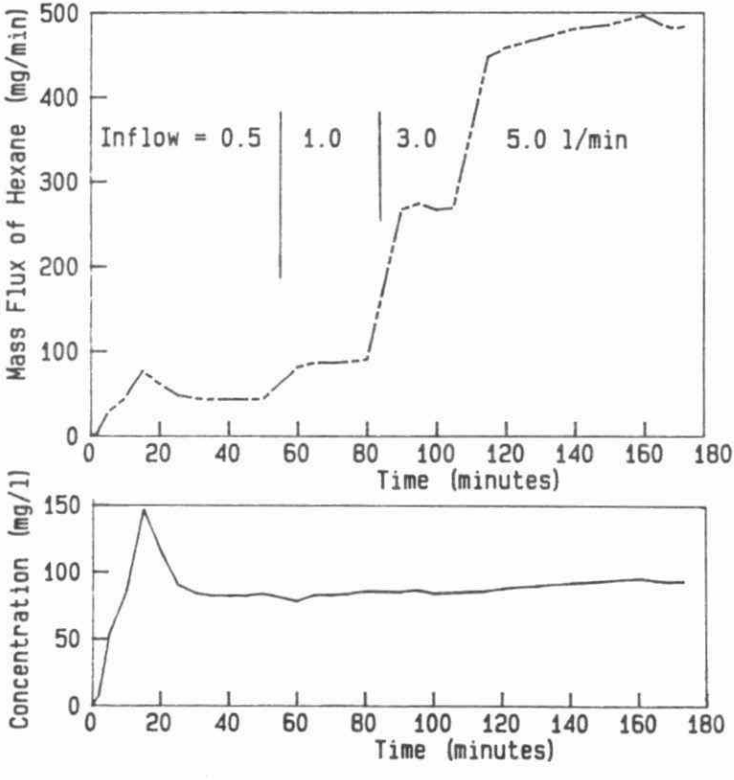


Figure 4: Exhaust concentration and mass loss rate of hexane for 4.8 cm dia. confined plug (variable inflow, 0.5 to 5.0 l/min).

separate experiments are plotted in Figure 5, showing the mass removal rate of hexane verses time, for 4.8 *cm* diameter contaminant plugs of heights 48 *cm* and 72 *cm*, and air inflows of 1.0 and 3.0 l/min. The results show that the mass removal rate increases with air flow, however the actual concentration of hexane in the exhaust vapour decreases with increased air flow. Also, the concentration of hexane, and as a result the mass removal rate, increases with the axial height of the zone of contamination, for a given air flow. The actual hexane concentrations for these experiments were greater than those measured during the previous experiments, where hexane removal was due solely to air flow within the zone of contamination. In these latter experiments, there is additional removal due to outward migration of hexane into air passing along the perimeter of the contaminant plug. However, the resulting concentrations are still substantially less than the theoretical equilibrium saturation.

3.3 Box Experiments

A series of experiments were performed in the large box in order to observe the phenomena studied in the column experiments on a larger scale, and to consider the effects of another dimension in the analysis. The experimental variables were air flow rate and the dimensions of the chemical residual source, which was hexane.

As in the column experiments, the hexane was poured into a form packed within the sand, so that the shape and dimensions of the resulting zone of residual contamination would be known. In this case, the form was a specially fabricated open–ended stainless steel box, with dimensions 90 *cm* high by 30 *cm* long by 5 *cm* wide. This box was constructed in such a way that each side could be removed independently, therefore minimizing the disturbance to the chemical source. The resulting zone of residual contamination had a length of 30 *cm* and a cross–sectional width of 5 *cm*, and the height was determined by the volume of hexane. In the experimentation, hexane volumes of 336 *ml*, 505 *ml*, and 673 *ml* were used which, based on a residual content of 72 *ml* per litre of sand, would result in heights of 31 *cm*, 47 *cm*, and 62 *cm*, respectively.

Air flow in the box was induced by negative pressure created with a vacuum pump. Air flow rates of 6.6, 13.2, and 26.4 l/min were used for the experimental runs, corresponding to specific discharges of 3.6, 7.2, and 14.5

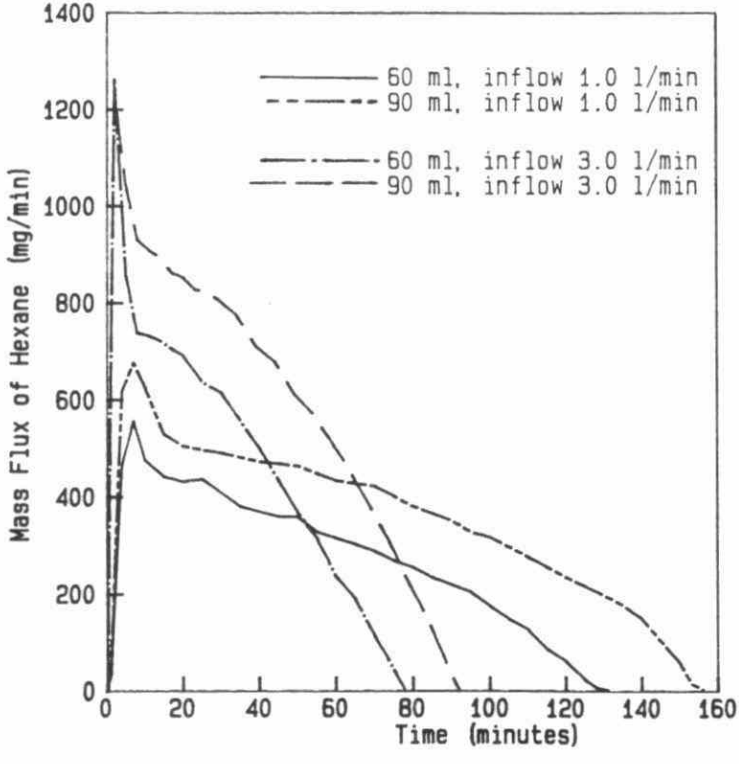


Figure 5: Mass loss rate of hexane for 4.8 cm dia. plugs (inflows 1.0 and 3.0 l/min).

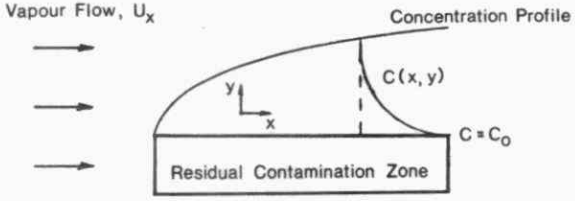


Figure 6: Development of concentration profile.

cm/min, respectively. Pressure measurements in the box indicated that flow through the chemical source was essentially horizontal and uniform.

Examination of the resulting relationship between hexane mass removal rate and time showed the same trends as were observed in the column experiments. Results will be presented in the following section.

4 Model Development and Simulations

After the completion of the laboratory experimentation, the second part of this study was directed towards developing a method to mathematically predict the vapour concentrations in the exhaust air. Ideally, this formulation would apply not only to the experimental work, but also would have wider applications in soil venting.

Based on experimental evidence, it was concluded that incoming air passing through the zone of residual contamination would emerge at equilibrium saturation with respect to the chemical source, in this case hexane. It then remained to predict the additional chemical removal due to air passing along the periphery of the contaminant zone. The problem was conceptualized as a boundary layer problem, illustrated in Figure 6.

Air passing along the contaminant zone is initially free of chemical vapours, however a concentration boundary layer develops due to vapour phase diffusion perpendicular to the direction of air flow. Assuming a constant concentration C_o at the surface, the steady-state mass transfer equation can be

written as (Brodkey and Hershey, 1988):

$$U_x \frac{\delta C}{\delta x} + U_y \frac{\delta C}{\delta y} = D \frac{\delta^2 C}{\delta y^2} \tag{1}$$

U_x : vapour velocity in x-direction ($\frac{L}{T}$)

U_y : vapour velocity in y-direction ($\frac{L}{T}$)

C : concentration of chemical in vapour phase ($\frac{M}{L^3}$)

D : diffusion coefficient ($\frac{L^2}{T}$)

For this analysis, it was assumed that the vapour velocity through the zone of residual contamination was equal to the vapour velocity through the surrounding sand. Experimentation showed that the vapour phase conductivity in the residual zone was only 5% less than the conductivity in surrounding sand, so this assumption should have introduced little error. In this case, the velocity in the y-direction was assumed to be zero, and the mass transfer equation reduced to:

$$\frac{\delta^2 C}{\delta y^2} - \frac{U_x}{D} \frac{\delta C}{\delta x} = 0 \tag{2}$$

Boundary conditions were set as follows:

for $x > 0$: $C = C_o$ for $y = 0$ and $C = 0$ for $y = \infty$

for $x = 0$: $C = 0$ for $y > 0$

This problem has the same form as one-dimensional transient heat transfer in a semi-infinite slab, and the solution can be written as (Brodkey and Hershey, 1988; Tikhonov and Samarski, 1963):

$$C(x, y) = C_o[1 - erf(\frac{y}{2\sqrt{\alpha x}})] \tag{3}$$

where α is a constant equal to D/U_x.

This formula was incorporated into a computer model to simulate the experimental conditions. It was assumed that the portion of the total air flow passing through the zone of contamination would emerge at saturation. This saturation concentration was calculated using the vapour pressure of the chemical at the appropriate temperature and pressure, and the ideal gas

law. Additional concentrations were calculated using Equation 3, with the appropriate diffusion coefficient and the air phase velocity calculated from the specific discharge and the porosity of the soil. Essentially, the model worked by calculating the concentrations at an instant in time, based on the dimensions of the contaminant zone, and then calculating the average chemical removal over a small time increment. The amount of chemical removed was then subtracted from the total mass, and the new dimensions of the residual zone were calculated. This process was continued in a time-step fashion until all the mass was removed.

The results of the model simulations for three experiments performed in the box are shown in Figure 7, as well as the experimental data. These results are for contaminant zones of three different heights, vented at a constant flow rate. The model results show reasonably good agreement with the experimental results.

5 Discussion

The results obtained from these experiments indicate that it may be reasonable to assume equilibrium saturation concentrations in exhaust gases from soil venting, but only when all the air passes through the zone of contamination. This is unlikely to be the case in most field situations. Experimental results, and subsequent analysis, for cases where there is air flow around a simulated contaminant spill have led to a predictive relationship for mass removal that appears to be promising. This formulation relies on the equilibrium vapour saturation concentration of the contaminant, the air phase velocity, and the appropriate diffusion coefficient. To date, good simulations of laboratory experiments have been accomplished, however this analysis requires that the shape and dimensions of the contaminant zone be known, an unlikely circumstance in field applications.

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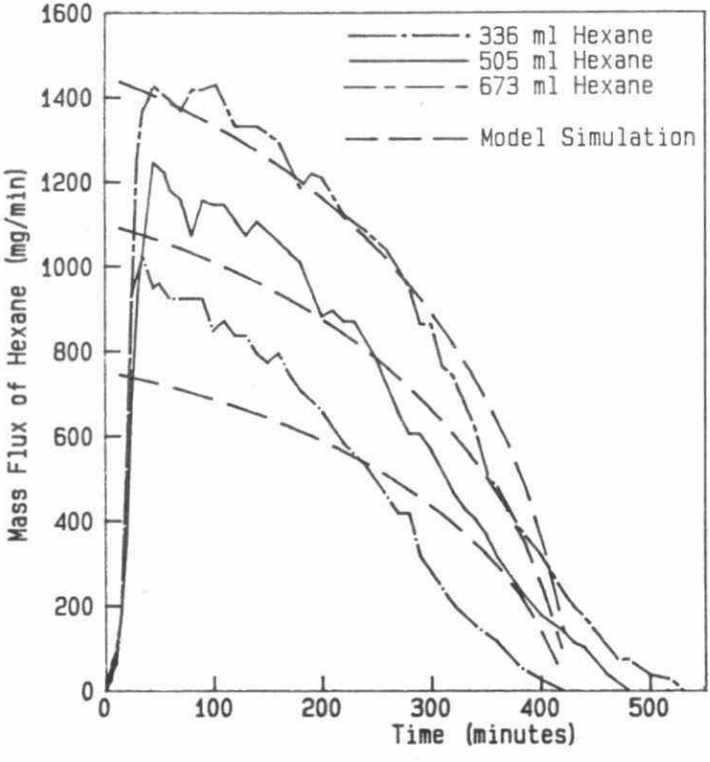

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COMPATIBILITY OF LEDA CLAY WITH MUNICIPAL SOLID WASTE LEACHATE

R.M. Quigley, F. Fernandez and C. Ohikere

Geotechnical Research Centre
Department of Civil Engineering
The University of Western Ontario
London, Ontario, N6A 5B9

ABSTRACT

Four Leda clay samples from the Ottawa/Carleton region were permeated with municipal solid waste leachate to assess their mutual compatibility using hydraulic conductivity, **k**, as the assessment tool. Three soft, unweathered samples were tested undisturbed at stresses less than the preconsolidation pressure and one sample of weathered clay was tested after recompaction.

All four specimens contained K^+ collapsible vermiculite which collapsed to illite during leachate permeation. The weathered clay actually underwent a 48% drop in cation exchange from 33 to 17 meq/100 g. In spite of the changes in mineralogy, the presence of effective stresses on the samples induced enough "chemical" consolidation to counter the adverse effects of chemical interaction. The result was a slow decrease or a constant **k** during testing.

Leachate saturation induced continuous consolidation creep throughout permeation that was not observed during water permeation at stress levels less than the preconsolidation stress.

INTRODUCTION

Leachate solutions generated by rainwater infiltration into and through various types of waste must be compatible with the liner (synthetic or natural) used to retain the waste. Should chemical interaction destroy the liner, leachate would escape into the local ground water possibly destroying a vital local resource.

This paper summarizes the results of a project carried out to assess the compatibility of Leda clay from the Ottawa/Carleton region of Ontario

with typical domestic waste leachate. Measurement of hydraulic conductivity was the assessment tool. The work was in the nature of a contract and was carried out as Project #299PL.

The terms of the contract required testing of four typical Leda clay samples and selection of these samples was the most difficult part of the project. The final four samples consisted of two soft clay samples from Candidate Site #10, one stiff sample from Site #19 and one weathered and fissured surface sample from the grounds of the National Research Council of Canada.

Domestic waste leachate from the Westminster Landfill site near London, Ontario was used as the influent permeant for the hydraulic conductivity tests.

For a complete description of this project, the interested reader is referred to our final report to the Ministry of the Environment dated July 14, 1989.

RESIDUAL SOIL CONDITIONS

A map of the Ottawa region taken from Crawford and Eden (1965) is presented on Figure 1. The locations of the three sites from which the clay samples were obtained are shown by the solid triangles. Site #10, which is most distant from Ottawa, is a candidate site; Site #19 was a possible energy-from-waste site; and Site #E is at NRC. The letters A to K on the map and the underlying profile refer to study locations discussed by Crawford and Eden.

The small scale cross-section illustrates the probable erosion in the area. Generally speaking, in low elevation areas of extensive erosion the clays are stiff and heavily preconsolidated compared to soft normally consolidated clays in uneroded areas. These trends are discussed in detail by Crawford and Eden (1965) and clearly show a trend of less preconsolidation and hence softer clays in higher elevation regions.

DESCRIPTION OF TEST SOILS

Physical Properties

The two Site #10 samples consisted of soft, grey, sensitive, silty clay from depths of 3.8 and 11.5 m. A thin sand cover at this site appears to have prevented extensive desiccation resulting in soft clays with high water contents of 55 and 67%, both exceeding their corresponding liquid limits of 51 and 65% (Table 1). Consolidation curves for these two samples are presented on Figure 2a and b. Both curves are S-shaped

indicating sensitive soils prone to large settlements if stressed beyond the two rather low preconsolidation pressures of ~ 55 and ~ 80 kPa. This clay demonstrated variations in water content of up to 50% over vertical intervals of only 2 or 3 cm. This was caused by invisible laminations related to deposition of silt or flocculated clay from overflow currents (Quigley, 1980).

The Site #19 sample was a grey silty clay from 3.3 m depth with a water content of 48% (close to its liquid limit of 49%). The consolidation curve on Figure 2c indicates a preconsolidation pressure of 214 kPa suggesting significant erosion in this area.

The Site #E sample consisted of a fissured, blocky, weathered, greyish clay from only 1.14 m depth, having a water content of 35%. The corresponding liquid limit was a high 70%, strongly suggesting the presence of swelling minerals. The consolidation curve for a wetter specimen from 1.26 m (Figure 2d) is a broad flat curve characteristic of overconsolidated clay.

Mineralogical and Porewater Characteristics

The x-ray powder patterns (not presented) and the traces for pressure oriented whole soil samples on Figure 3 indicate that all four samples contain abundant quartz, moderate to abundant feldspar, and moderate amounts of illite. Carbonate comprises 3 to 7.5% of the Site #10 and Site #19 samples but appears to have been leached out of the Site #E sample. Chlorite is present in moderate amounts in the Site #10 samples, in trace amounts in the Site #19 sample, and completely absent from the Site #E sample. Minor to trace amounts of swelling clays were present in the samples from Sites #10 and #19. The Site #E sample, however, contained abundant swelling clay, probably produced by oxidation weathering of original chlorite normally found in Leda clay but absent from the Site #E sample. A summary of the qualitative mineralogy is presented in Table 2.

The porewater chemistry is also presented in Table 2. The two Site #10 samples are dominated by Na^+ at salinities of 1.5 and 6.5 g/L. The Site #19 sample has been leached free of salts having a salinity of only 0.3 g/L. The leached NRC sample had a salinity of 1.5 g/L and was dominated by calcium in the pore water. The calculated sodium adsorption ratios (SAR) varied from 1 to 7 for the low salt clays increasing to 23 for the saline soil from 11.5 m depth at Site #10.

DESCRIPTION OF LEACHATE

The test leachate collected from the Westminster Landfill site in April 1988 was divided into two portions, one to study leachate stability and the other for use as the influent permeant. The composition of the leachate just prior to the first permeation run was as follows:

Item	Concentration (mg/L except pH)
pH	6.9
Chloride	1323
Sodium	647
Potassium	372
Calcium	247
Magnesium	280
Iron	66

Potassium is an important constituent since the swelling clay component of Leda clays is subject to c-axis contraction caused by K^+ fixation. Ammonium (NH_4^+) acts in a similar way but was not measured.

Raw leachate is a very unstable material probably because of bacterial activity. Ca^{++} precipitates as $CaCO_3$ and Fe^{++} precipitates as amorphous FeS_2 forming black slimy flocs (Yanful, Fernandez and Quigley, 1987). The resulting reductions in influent Ca^{++} and Fe^{++} must be monitored along with the effluent chemistry so they are not confused with legitimate interactions between the test clays and the leachate.

METHODS

A computer controlled, constant flow rate, fixed ring permeameter was used for the study. A low vertical effective stress of 40 kPa was used so that the soft soils would not be overstressed (if possible).

A very slow flow rate of 15 to 20 x 10^{-5} mL/s was employed so that the seepage drag forces at the base of the samples would be as small as possible. A displacement rod enabled measurement of consolidation during both static loading and seepage drag loading during permeation.

The three Site #10 and #19 samples were tested "undisturbed" to represent field conditions. The stiff fissured clay from Site #E was so pervious that it had to be slurried and compacted into the permeameter to lower the hydraulic conductivity to a value characteristic of the mineralogy rather than the fissured soil structure.

The influent and effluent chemistry was monitored and the k-tests run until the effluent values of potassium, which was highly retarded, had reached influent values thus indicating equilibrium.

Post-testing assessment involved x-ray diffraction on pressed pellets

of soil from the actual k-tests and cation exchange capacity measurements to explain the significance of major changes in the x-ray traces.

Details of the methods are presented in the final report.

RESULTS

Reference Hydraulic Conductivity with Water

The results of the reference k-testing, using 0.01 N $CaSO_4$ in distilled water as the permeant, are presented on Figures 4 to 7, inclusive. Each figure contains a plot of hydraulic conductivity, k, and settlement, ρ, vs pore volumes passed through.

The Site #10 sample from 3.82 m depth yielded k = 3.5 x 10^{-8} cm/s using a flow rate of 8.9 x 10^{-5} mL/s. At this rate, the total static + drag stress at the base of the sample was 42 kPa which is below the σ_p' = 55 kPa. As a result the settlement caused by seepage was minimal as shown by the settlement curve. The initial settlement due to the static loading of 40 kPa was 0.396 mm which was about 2% of the 20 mm sample thickness. This settlement results from sample disturbance and is inevitable for sensitive clays. Increasing the flow rate to 44.5 x 10^{-5} cm/s increased the maximum effective stress to 60 kPa (40 static + 20 seepage) causing some settlement and a small decrease in k to 1.95 x 10^{-8} cm/s.

Similar patterns of settlement and hydraulic conductivity may be observed for all four test specimens on Figures 4 to 7. On the basis of these tests the flow rates for leachate permeation were kept below 20 x 10^{-5} mL/s.

The reference k-test values and the corresponding void ratios of the test clays were as follows:

Sample Number and Depth	Void Ratio	Reference k (water) cm/s
10-3-WOF (3.82 m)	1.484	1.95 x 10^{-7}
10-2-WOE (11.51 m)	1.723	6.4 x 10^{-8}
19-1-3 (3.29 m)	1.369	1.8 x 10^{-7}
#E (NRC) (1.14 m)	0.978	6.05 x 10^{-9}

These data are plotted on the summary plot as open circles on Figure 12.

Hydraulic Conductivity with Leachate

The results of the leachate compatibility k-tests are presented on Figures 8 to 11, inclusive. These tests were run on different specimens containing the original pore water. Three of the tests (Figures 8, 9 and 10) were run in two steps with a 10-day no-flow period between them. The purpose was to allow the test on smectitic Sa #E to catch up and to assess any creep effects in the Site #10 soils which would be loaded to or beyond σ_p' if a landfill is built on them. As noted previously all tests were terminated when the effluent K^+ reached influent values, indicating equilibrium.

The deep sample from Site #10 (Figure 9) and the stiff sample from Site #19 (Figure 10) both display a long slow decrease in k over the 11.5 pore volumes of leachate permeation. This decrease is accompanied by a slow creep consolidation shown by the settlement curves. Since both of these specimens were overconsolidated relative to the total static and seepage stresses on the samples, this creep is attributed to chemical interaction with the MSW leachate. The 10-day resting period had little effect on the test results.

The shallow sample from Site #10 (Figure 8) was subjected to a maximum static plus seepage stress of 55 kPa which is approximately equal to the preconsolidation pressure. During the initial permeation of 6.8 pore volumes of leachate, a slow decrease in k may be observed, even though the settlement had stopped. The 10-day resting period caused a significant increase in consolidation once permeation was recommenced. This was accompanied by a corresponding decrease in k.

The smectitic Site #E sample (Figure 11) shows an almost constant k value for the entire 9.2 pore volumes of leachate flow despite a large amount of settlement and reduction in void ratio. This unusual behaviour is related to a large decrease in cation exchange capacity discussed later.

In summary, the final void ratios and the corresponding value of hydraulic conductivity for the leachate permeated samples are tabulated as follows:

Sample Number and Depth	Void Ratio	Final **k** (leachate) cm/s
10-3-WOF (3.86 m)	1.187	2.5×10^{-8}
10-2-WOE (11.57 m)	1.544	4.3×10^{-8}
19-1-3 (3.10 m)	1.397	3.9×10^{-8}
#E (NRC) (1.12 m)	0.966	3.6×10^{-9}

Discussion

Since all of the **k**-tests started and terminated at different void ratios, comparison of any clay/leachate interaction trends are most likely to appear on a summary plot of void ratio vs **k**. Such a plot is presented on Figure 12 which clearly shows a trend of lower **k** vs void ratio for the leachate-permeated specimens than the water-permeated specimens.

EFFLUENT CHEMISTRY

In the final report, plots of effluent chemistry vs pore volumes are presented for all four tests for pH, Cl^-, Fe, Na^+, K^+, Ca^{++} and Mg^{++}. For this paper, only a very brief description is presented.

For all four tests, K^+ was strongly retarded. About 6 PV of flow was required for the two Site #10 samples and about 10 PV for the Site #19 and #E samples. For Sa #E (NRC), the potassium did not even appear in the effluent until after 2 PV of flow.

Adsorption of K^+ by all samples and adsorption of Mg^{++} by Sa #E (NRC) results in desorption of other species. This desorption, if intense enough, appears as a hump on the effluent curves which is equivalent to a hardness halo. Sa #10-3-WOF displayed a Mg^{++} halo; Sa #10-2-WOE showed a slight Mg^{++} halo and a prolonged Na^+ removal; Sa #19-1-3 showed a strong Ca^{++} halo; and Sa #E (NRC) displayed a very strong Ca^{++} halo.

Some of these trends are reflected in the post-testing assessment chemistry.

POST-TESTING ASSESSMENT

X-ray diffraction traces obtained on pressed pellets of whole soil samples from Sa #10-3-WOF (3.86 m) and Sa #E (NRC) are presented on Figures 13 and 14. The Site #10 sample (Figure 13) contains some vermiculite/smectite in its natural state which collapsed to illite on exposure to leachate (reduction in height of the 1.47 nm peak and increase in height of the 1.0 nm peak). The Site #E sample contains abundant vermiculite/smectite (1.52 nm peak) and abundant interlayered illite/smectite (1.24 nm peak) in the natural state. As shown by the traces on Figure 14, both these species literally disappear on leachate permeation due to K^+ fixation.

A summary plot of the 1.5/1.0 nm peak height ratios is presented on Figure 15 as a rough guide to the magnitude of the collapse. Sa #E (NRC) has obviously undergone a large change in mineralogy relative to the other three samples as a result of leachate permeation.

As a final check on the intensity of collapse, the CEC values are compared before and after leachate permeation as follows:

Sample Number and Depth	Cation Exchange Capacity, meq/100 g		Δ CEC
	Natural	Leachate	
10-3-WOF (3.86 m)	14.0	15.6	+ 1.6
10-2-WOE (11.57 m)	28.2	21.9	- 6.3
19-1-3 (3.10 m)	22.7	19.8	- 2.9
#E (NRC) (1.12 m)	31.8	17.5	-14.3

The CEC values changed very little for the Site #10 and #19 samples indicating only minor mineralogical alteration as a result of leachate permeation. The CEC of the Site #E (NRC) sample decreased significantly from ~ 32 meq/100 g (natural) to 18 meq/100 g (leachate). This large decrease in CEC translates into a loss of double layer cations and double layer water and explains the large amount of consolidation during leachate permeation without a corresponding decrease in **k**.

Discussion

Most of the southern Ontario clayey soils studied to date have exhibited only modest c-axis contraction and K^+ fixation as a result of

permeation with normal domestic leachate, at least in the wet state (Quigley et al, 1988). The charge deficiency of the swelling clay component seems to be borderline between smectite and vermiculite (-0.5 to -0.6/unit cell of 10 oxygens). As a result, the swelling clay collapses extensively in the presence of dilute KCℓ if air dried but not if kept water-wet or leachate-wet as is the case for an operating liner or natural barrier.

The significant contraction of the leachate-wet swelling clays found in the four Ottawa/Carleton Leda clay samples seems to be something new, especially the phenomenal collapse of the Site #E (NRC) samples. This collapse, clearly visible on the x-ray traces, was confirmed by special chemical analyses which showed a decrease in CEC from 32 to 17½ meq/ 100 g for the weathered, vermiculitic Site #E sample.

The above discussed K^+ fixation and collapse phenomena occurred at a K^+ concentration of only 372 mg/L (0.01 N) in the Westminster leachate. This seems to be a fairly normal value for southern Ontario leachate. Ammonium (NH_4^+) is also common in leachates at concentrations up to 1000 mg/L. It is about the same size as K^+ and also serves to collapse vermiculite.

K^+ and NH_4^+ fixation and c-axis contraction seem, therefore, to be phenomena which must be considered for Leda clays in the Ottawa/Carleton region. For most very stiff to hard compacted clays, a trend towards an increased **k** should result if the soils remain at constant void ratio. For the Ottawa/Carleton Leda clays, the net result of leachate permeation seems to have been a decrease in bond strength between the particles which caused creep consolidation in excess of that observed for permeation of water. The gradually decreasing void ratio caused a corresponding decrease in **k**, compensating for any physico-chemical factors that might normally cause an increase in **k**.

The influence of leachate saturation on other engineering properties of Leda clay such as shear strength and compressibility are beyond the scope of this paper.

CONCLUSIONS

Four Leda clay samples of widely varying composition and physical properties have been permeated with domestic waste leachate to assess their mutual compatibility, using hydraulic conductivity, **k**, as the assessment tool. The major conclusions of the study are as follows:

1. The hydraulic conductivity of all samples decreased as a result of leachate permeation. This decrease in **k** was in spite of K^+ fixation and c-axis contraction of soil vermiculite to illite.

2. An inferred effect of leachate permeation was an apparent weakening of the structure of the Leda clay resulting in continuing creep consolidation during seepage not observed for water permeation. This creep had not terminated at the end of testing as it had for water. The effects of saturation of Leda clay by domestic waste leachate on shear strength and compressibility remain to be defined.

3. All samples are believed to have been close to chemical equilibrium with the influent leachate since effluent concentrations had reached influent values when the tests were terminated.

4. The decreases in **k** seem most significant at high void ratios (1.2 to 1.6).

5. The weathered vermiculitic Leda clay from Site #E (NRC) also demonstrated creep consolidation during leachate permeation, even at a relatively low void ratio of 0.98. K^+ fixation and c-axis contraction resulting in a decrease in volume of the solids phase probably caused most of this creep during which **k** remained remarkably constant.

ACKNOWLEDGEMENTS

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We also acknowledge the assistance of Geocon Inc. and MacLaren Engineers Ltd. who did the soil sampling at Sites #10 and #19 and Dr. K.T. Law at the Institute for Building Research at the National Research Council of Canada who generously supplied us with a weathered near surface Leda clay sample.

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Table 1. Physical Characteristics of Test Soils

Sample	Site #10		Site #19	Site #E
Item	3.82 m	11.51 m	3.29 m	1.14 m
Borehole No.	10-3	10-2	19.1	N/A
Sample No.	WOF	WOE	3	N/A
Elevation (m)	72.05	64.76	66.38	93.41
Water content, ω_n (%)	55	67	48	35
Liquid limit, ω_L (%)	51	65	49	70
Plastic limit, ω_p (%)	23	29	22	35
Plasticity index, Ip	28	36	27	35
Preconsolidation Pressure, σ'_p (kPa)	~ 55	~ 80	~ 214	100-300
Max. Comp. Index, C_c(max)	0.76	0.62	0.69	0.36
Permeability at σ'_v = 40 kPa (cm/s)	20×10^{-8}	6.4×10^{-8}	18×10^{-8}	(1) 48×10^{-8} (2) 0.6×10^{-8}

Notes: (1) Compacted fissured sample
(2) Compacted slurried sample.

Table 2. Mineralogical and Chemical Characteristics of Test Soils

Sample	Site #10		Site #19	Site #E
Item	3.82 m	11.51 m	3.29 m	1.14 m
Sample Number	10-3-WOF	10-2-WOE	19-1-3	E-NRC
Mineralogy:				
Quartz	Abund	Abund	Abund	Abund
Feldspar	Mod	Mod	Mod-Minor	Abund
Carbonate(1) (%)	6.1	3.0	7.5	0.2
Illite	Mod	Mod	Mod	Mod
Chlorite	Mod	Mod	Tr	Nil
Smectite/Vermiculite	Tr	Tr	Minor	Abund
Pore Water:(2)				
pH	8.1	8.1	8.2	7.0
Salinity,(3) mg/L	1,500	6,500	300	1,400
Na^+ (4) "	285	1,500	32	335
K^+ "	15	57	11	15
Ca^{++} "	34	43	45	350
Mg^{++} "	61	185	33	38
Chloride(5) "	634	3,555	14	1,859 ?
SAR(6) $(meq/L)^{\frac{1}{2}}$	- 7	- 23	- 1	- 5

Notes: (1) Carbonate by gasometric analysis.
(2) Pore water squeezed from samples at 10 and 17 MPa.
(3) Salinity by conductivity and reference to NaCℓ standards.
(4) Cations by atomic adsorption spectrometry.
(5) Chloride by specific ion electrode.
(6) SAR = Sodium adsorption ratio.

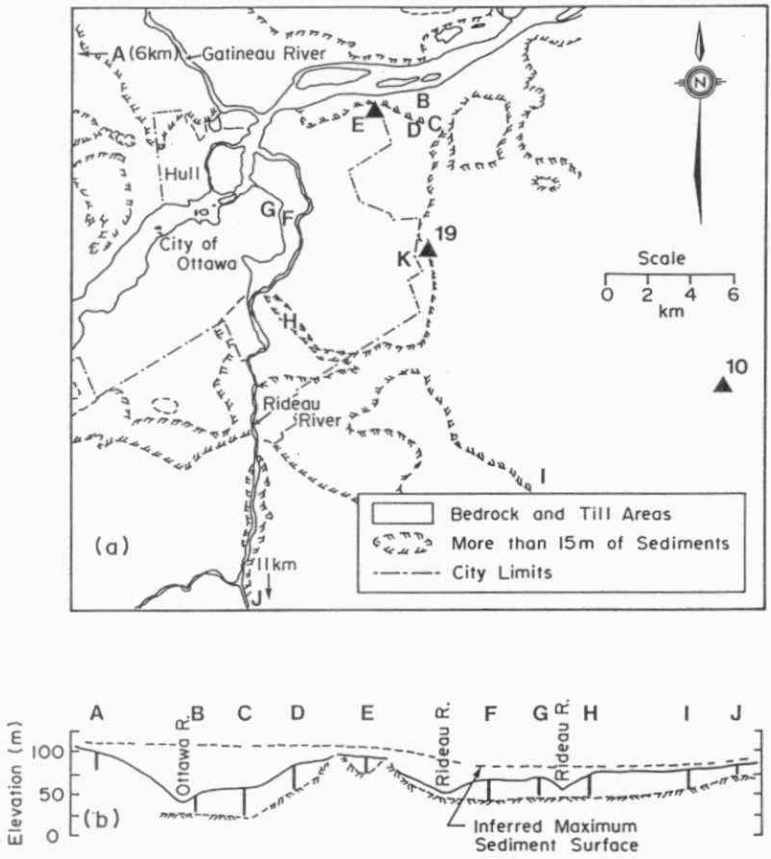


FIGURE 1. (a) OTTAWA-CARLETON REGION MAP SHOWING LOCATIONS OF NRC STUDY BORINGS (A TO K) AND THE UWO STUDY SITES (▲); (b) GENERALIZED CROSS-SECTION

[Adapted from Crawford and Eden, 1965]

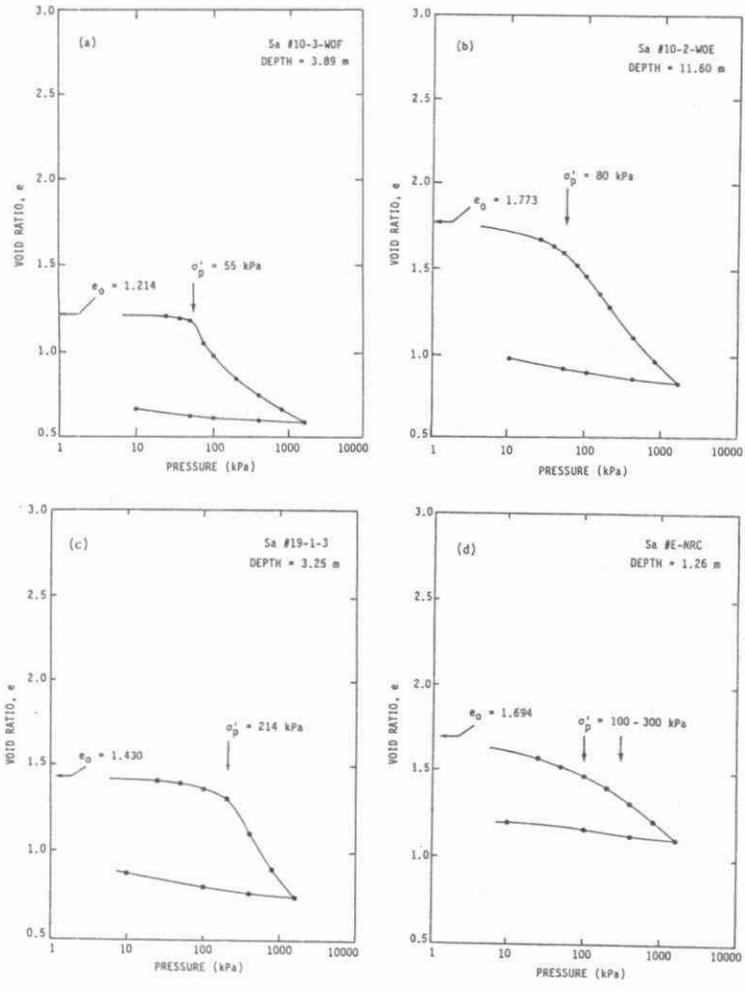


FIGURE 2. CONSOLIDATION CURVES OBTAINED ON TEST SPECIMENS: (a) Sa #10-3-WOF AT 3.89 m; (b) Sa #10-2-WOE AT 11.60 m; (c) Sa #19-1-3 AT 3.25 m; (d) Sa #E(NRC) AT 1.26 m

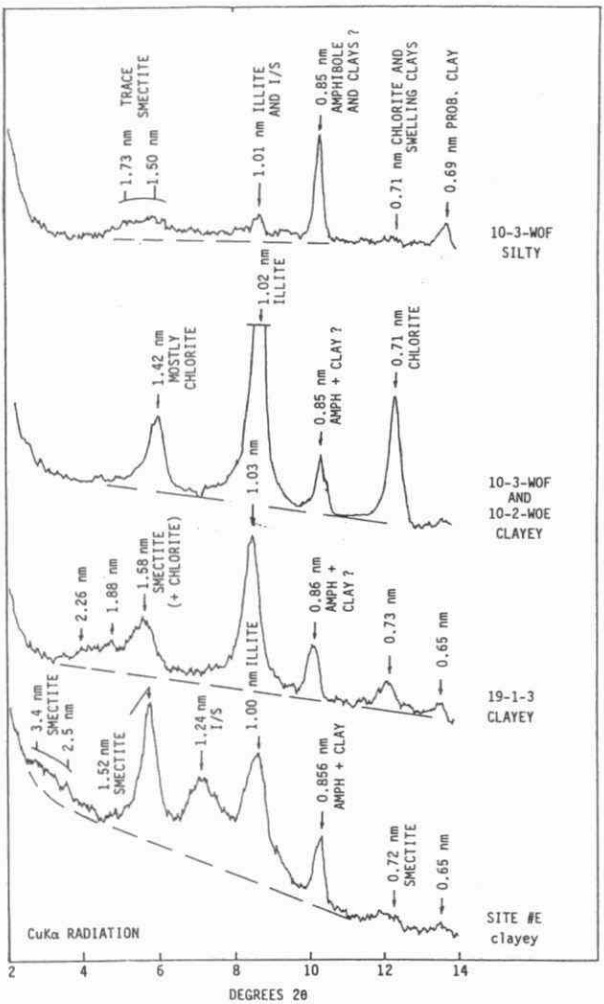


FIGURE 3. X-RAY TRACES OF WATER-WET, WHOLE SOIL TEST SAMPLES, PRESSURE ORIENTED AT 120 kPa

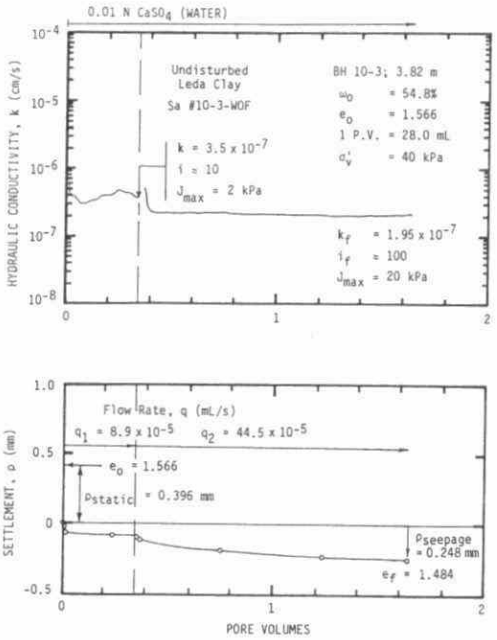


FIGURE 4. HYDRAULIC CONDUCTIVITY AND SETTLEMENT VS PORE VOLUMES; SITE 10, BH #10-3, 3.82 m DEPTH. REFERENCE PERMEANT: 0.01 N $CaSO_4$ SOLUTION IN WATER

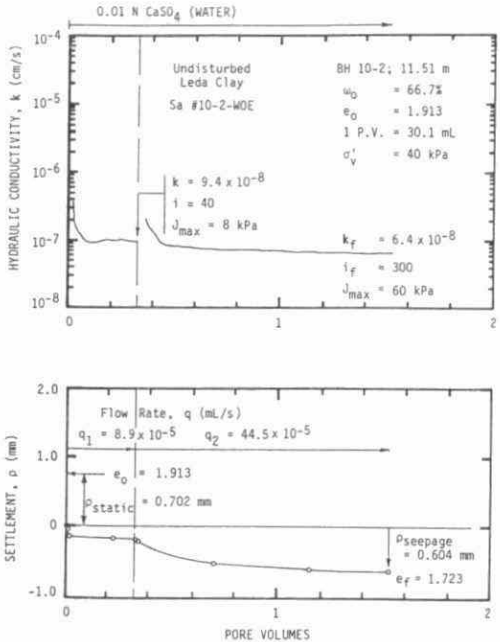


FIGURE 5. HYDRAULIC CONDUCTIVITY AND SETTLEMENT VS PORE VOLUMES; SITE 10, BH #10-2, 11.51 m DEPTH. REFERENCE PERMEANT: 0.01 N $CaSO_4$ SOLUTION IN WATER

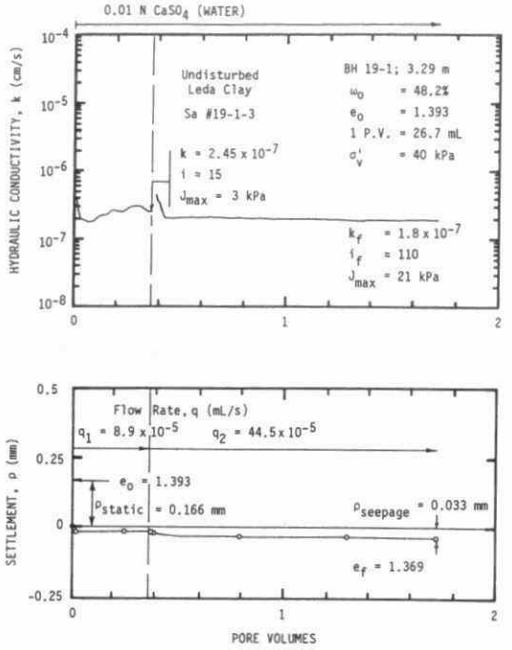


FIGURE 6. HYDRAULIC CONDUCTIVITY AND SETTLEMENT VS PORE VOLUMES; SITE 19, BH #19-1, 3.29 m DEPTH, REFERENCE PERMEANT: 0.01 N $CaSO_4$ SOLUTION IN WATER

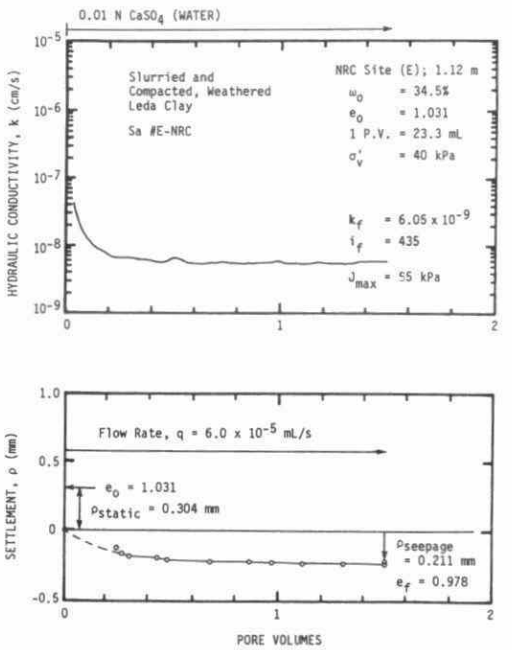


FIGURE 7. HYDRAULIC CONDUCTIVITY AND SETTLEMENT VS PORE VOLUMES, NRC SITE (E), 1.12 m DEPTH, SLURRIED AND COMPACTED. REFERENCE PERMEANT: 0.01 N $CaSO_4$ SOLUTION IN WATER

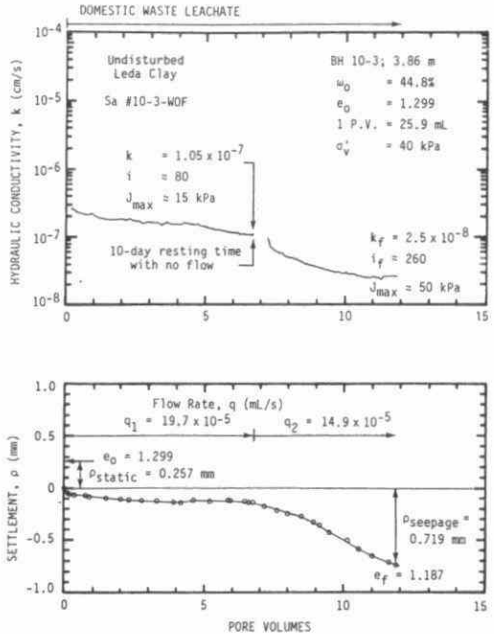


FIGURE 8. HYDRAULIC CONDUCTIVITY AND SETTLEMENT VS PORE VOLUMES; SITE 10, BH #10-3, 3.86 m DEPTH, PERMEANT: DOMESTIC WASTE LEACHATE

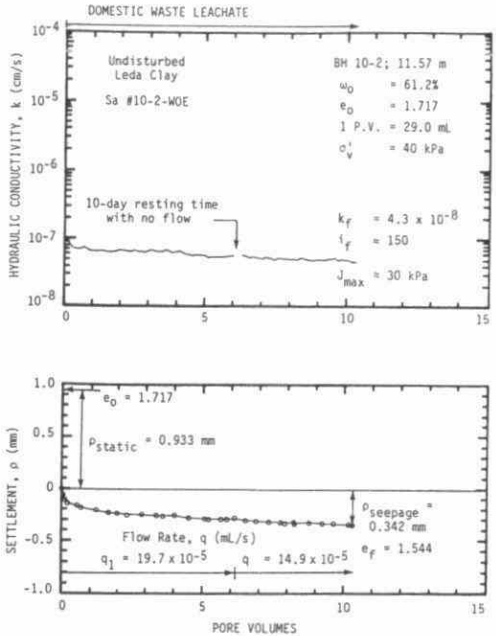


FIGURE 9. HYDRAULIC CONDUCTIVITY AND SETTLEMENT VS PORE VOLUMES; SITE 10, BH #10-2, 11.57 m DEPTH, PERMEANT: DOMESTIC WASTE LEACHATE

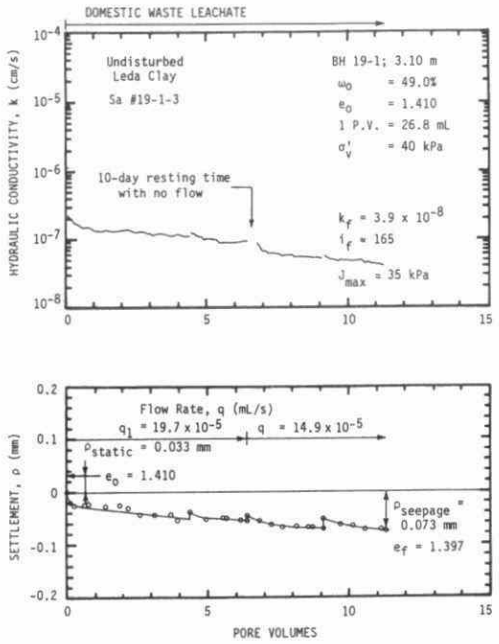


FIGURE 10. HYDRAULIC CONDUCTIVITY AND SETTLEMENT VS PORE VOLUMES; SITE 19, BH #19-1, 3.10 m DEPTH. PERMEANT: DOMESTIC WASTE LEACHATE

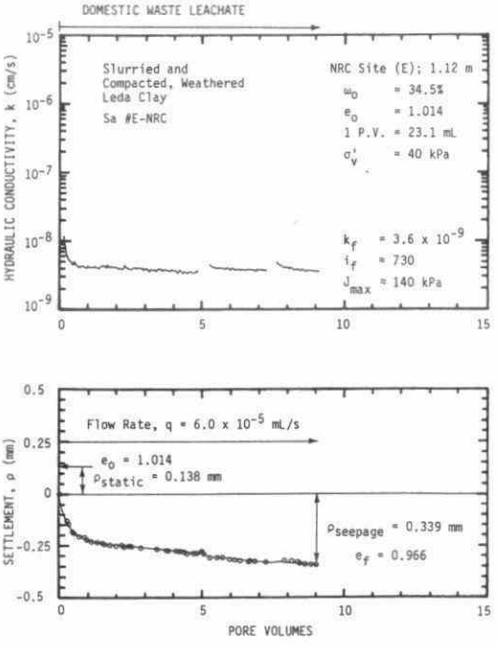


FIGURE 11. HYDRAULIC CONDUCTIVITY AND SETTLEMENT VS PORE VOLUMES; NRC SITE (E); 1.12 m DEPTH, SLURRIED AND COMPACTED. PERMEANT: DOMESTIC WASTE LEACHATE

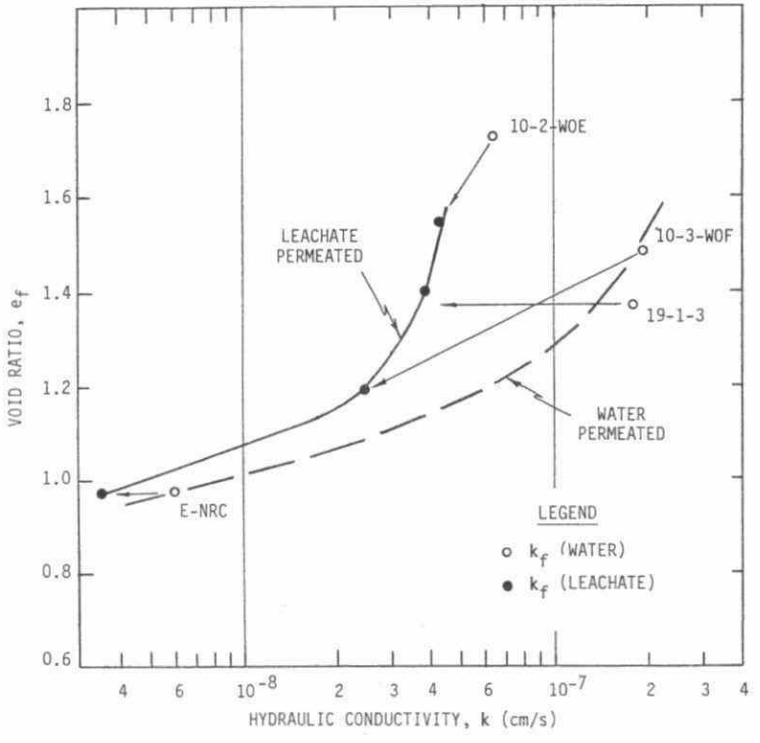


FIGURE 12. SUMMARY PLOT SHOWING EFFECT OF LEACHATE PERMEATION ON THE HYDRAULIC CONDUCTIVITY OF THE FOUR LEDA TEST CLAYS

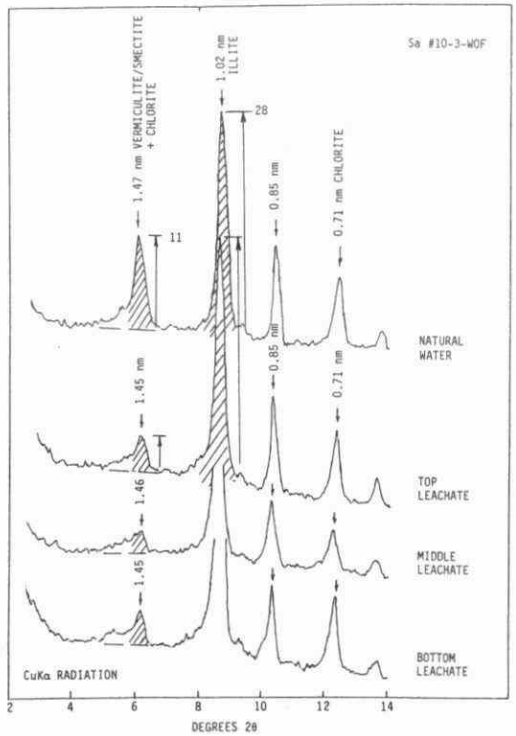


FIGURE 13. X-RAY TRACES OF PRESSURE ORIENTED, WHOLE SOIL SPECIMEN OF Sa #10-3-WOF, BEFORE AND AFTER LEACHATE PERMEATION

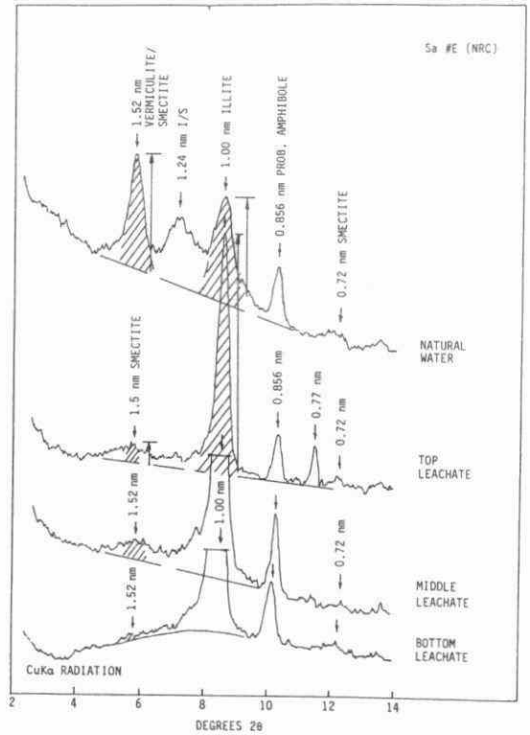


FIGURE 14. X-RAY TRACES OF PRESSURE ORIENTED, WHOLE SOIL SPECIMENS OF Sa #E (NRC)

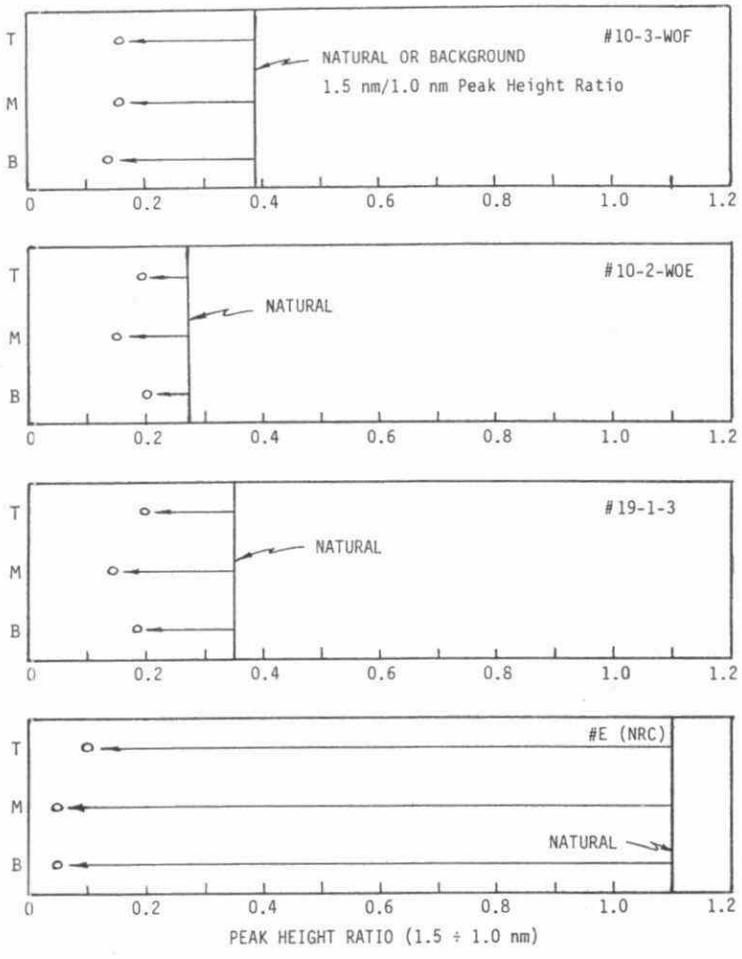


FIGURE 15. SUMMARY PLOT OF 1.5 nm/1.0 nm PEAK HEIGHT RATIOS SHOWING COLLAPSE CAUSED BY K^+ ADSORPTION AND FIXATION

[T, M, B = Top, middle and bottom of 20 mm thick test specimen]

C5

CODISPOSAL OF INDUSTRIAL WASTE WITH MUNICIPAL REFUSE AN EXAMINATION OF THE EFFECTS OF A HAZARDOUS WASTE

D.W. KIRK and S. PIRANI*, Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, Ontario M5S 1A4

INTRODUCTION

The use of landfill disposal continues to be the most widely used system for disposal of municipal refuse. Despite the long history of landfill use the impact of the landfill on the surrounding environment and aquifer remains controversial. Although the initial content of the landfill can be estimated with reasonable accuracy, the rate and extent of material transfer to the environment is not well defined. Part of the difficulty is in quantifying the parameters that control the chemical and biological reactions occurring within the landfill mass. Knowledge of these parameters is critical in determining environmental impact and in improving the design of long term landfill sites.

While field studies of existing landfills provide valuable information, there is little opportunity to modify controlling parameters to quantify their significance. On the other hand, laboratory studies generally have not been able to duplicate field behaviour and thus lack applicability for environmental modelling. This study has employed large scale laboratory leaching columns which were designed to simulate landfill behaviour. As a result of their size the columns are operated in an outside location. This scale of experimentation, though large for laboratory studies, is required for developing the landfill hydrodynamics and biological activity. Furthermore this size of study is suitable for testing and quantifying the effect of various parameters on leachate and gas generation. The parameters that were selected for study are; the role of moisture input and the role of a hazardous industrial waste on leachate contamination. The moisture input was in two forms. The first was with controlled water addition for mass balance determination, and the second was via atmospheric precipitation to investigate acid rain and evapotranspiration effects. The role of hazardous waste was studied using a selected hazardous waste at 8 and 30 weight percent of the municipal refuse content. The waste was added in layers in the test cells. The effect of hazardous waste in a landfill site is not well understood. Several studies have indicated little change of leachate quality with a variety of wastes. A serious concern with hazardous wastes is the long term behaviour in the landfill environment which undergoes through several phases before final stabilization. The effects of the hazardous wastes may not be apparent until the buffering capacity of the landfill is lost. The leachate quality of a variety of test cells has been studied over an extended period (4 years) and the effects of the hazardous waste addition to the test cells are examined.

EXPERIMENTAL

The column study, supported by the Ontario Ministry of the Environment was initiated to test the feasibility of simulating municipal refuse landfill conditions and to investigate the effect of a hazardous solid waste on the municipal refuse environment. The details of the column construction have been reported previously[1]. There are 16 columns in operation packed with 4 different compositions: 100% municipal solid waste(MSW), MSW + 8% industrial waste(IW), MSW + 30% IW and 8% IW in sand. The high density polyethylene cylindrical columns are 1.93m high, and 0.33m in diameter and contain approximately 43 kg (dry weight) of MSW. One half of the columns receive moisture input from precipitation while the other half receive controlled periodic water additions. The systems are maintained in unsaturated flow conditions with regular leachate removal from the bottom reservoirs. Results from three MSW columns, column numbers 1, 2 and 3, have been used in the comparison with small and large field cells [2]. This study is on-going and all the columns have been in continuous operation for over four years.

RESULTS and DISCUSSIONS

From previous work[2] we have demonstrated that the behaviour of our test cells containing municipal refuse is similar to that observed in medium and large field cell studies. The comparison was based on the concentration behaviour of 8 elements (Cu, Zn, Fe, Na, K, Cl, Mn, Mg), COD and pH. An effect of the size of the test cells was noted in which the smaller the cell used, the greater the initial concentration of the parameter measured. The differences in concentrations measured between the studies disappeared after the initial 2 year period. The similarity of concentration behaviour of the leachate in the studies allowed a common 1st order rate model to be used for concentration as a function of normalized leachate volume.

An example of a contaminant concentration that was modelled and compared with large field cell studies was zinc. This element is significant in our work because of the concentration (14 wt%) of the element in the industrial solid waste (Table 1). The LEP screening test did not reveal any significant extraction of the element from the waste. The concentration of zinc in the leachate from the municipal refuse columns is shown in Figure 1. The +/- 1 standard deviation from the leachate model is shown as two solid lines in the figure. As can be seen from the figure the test cell data displays typical variability but is generally bounded by one standard deviation from the model and there is a very good regression correlation coefficient (r=0.98) for the model. Landfill behaviour was similar though had lower initial values.

The concentration of zinc found in the test cells with 8% industrial waste is shown in Figure 2. For comparison the standard deviation lines for the MSW model are repeated but for the data on a time rather than a volume basis. Additional

variability due to moisture throughput occurs, but more readily allows the comparison with data from codisposal columns. The 8% IW with MSW data show a more rapid decline in leachate concentration than do the MSW data. The model cannot be adapted to fit the 8% IW with MSW data with an acceptable correlation coefficient. A statistical "F Test" of the two sets of data show the observed differences are significant(α= 0.05). The failure of the model and the significant differences in the leachate concentrations were not limited to zinc but were found for the elements Cu, Mn, Ca, Mg, Pb, Ni, Fe, Co and S. In all examples, the concentrations decreased more rapidly with time or leachate volume for the test cells with 8% IW than for those with only MSW. This behaviour is not predictable from LEP tests. One suggestion that has been made regarding layers of industrial waste in municipal refuse is that the waste may form an impermeable layer resulting in fluid channelling. If this process occurred in the test columns then the concentrations of all the elements should be affected. This is not observed. Figure 3 shows the concentrations of a readily leached species (sodium), for the MSW test cells (a) and MSW +8%IW test cells (b). There is no significant difference between the results. The other readily solubilized elements K, Br and Cl displayed the same behaviour as Na and the leachate from the columns with IW could not be distinguished from those with only MSW, based on analysis of the readily solubilized elements over the course of the study. Columns with 30% IW did show slightly elevated concentrations which was attributable to the additional burden of the elements in the IW.

In Figure 4, the concentration of zinc in the leachate is shown for columns having 30% IW. Since 8% IW had a significant effect on the concentration, the higher IW content would be expected to have an even greater effect. However, the concentration data for the 30% IW test cells appears to fall into either the MSW concentration profile or the 8% IW profile. The one standard deviation band for the MSW model and the average of the four 8% IW test cell data are shown on the figure for reference. This dual behaviour was typical for the leachate elements Ca, Cu, Fe, Mg, Pb, S, Zn, Co, Mn and Ni. Since the higher industrial waste content did not directly lead to a more dramatic change in the leachate chemistry, the factor controlling the leachate chemistry cannot be the presence of industrial waste.

In searching for factors which can be linked to the observed behaviour, the effect of moisture addition can be ruled out. There is no significant difference between the data from controlled water addition and from atmospheric precipitation over the time frame of this study, except for the volume of leachate generated. Moisture throughput affects the extent of leaching with time but not the contaminant concentration on a leachate volume basis.

Differences in Eh, the oxidation condition, among the test cells did not explain the IW leachate concentration behaviour but were found to be correlated with the pH differences.

The role of pH on the rate of metal leaching is well established. The average pH for the MSW columns is shown in Figure 5. The MSW leachate has consistently remained more acidic than the leachates from columns with industrial waste. The

leachate pH from the MSW columns has been slowly rising during the course of the study. In contrast the leachate from the 8% IW, after an initial excursion to a pH of 7.4 has been decreasing and both sets of data appear to be approaching a value of 6.4. The more heavily contaminated MSW columns (30% IW) again show a dual behaviour. Leachate from two of the columns follow the same concentration profile as the 8% IW columns, while the other two initially followed the MSW behaviour. With the approach to a common pH, all the leachates generally have produced low contaminant levels in the leachate. The more alkaline nature of the leachate from the IW columns is interesting since the acid generated by the biological waste degradation should have neutralized the alkaline IW long ago.

An 8% IW+MSW and a 30% IW+MSW sample were tested using a 5:1 water to solid ratio in a batch mode for one month. During that period, the initial alkalinity due to the industrial waste was acidified in the 8% sample and the 30% IW sample had been reduced from an initial pH of 12 to 7.5. The acidification is directly associated with biological activity. Thus neutralization of the industrial wastes in the test cells should have taken place during the field capacity stage. The early leachate pH values from all the test cells were acidic as would be expected.

The association of acidification with biological activity is readily observed from the COD behaviour as shown in Figure 6. The columns with the more acidic leachate (MSW behaviour) have shown and maintained higher COD production rates than the other columns. Again the MSW columns and the 8% IW columns have shown different leachate behaviour while two of the 30% IW columns have followed the MSW pattern while the other two have followed the 8% IW pattern. Although the COD production in all columns is now relatively low, there are still organic acids being produced in the leachates and methane being detected in the gas. Although the leachate contaminant concentrations may be linked to pH and COD levels, the role of the IW on the leachate chemistry is not yet understood.

There have been suggestions in the literature that when the buffering capacity of the landfill is lost, then there may be an increase in the concentration of metal ions in the leachate. Although our test cells have not yet biologically stabilized there has been observed over the last year, a rise in the concentration of certain elements most notably Cd, Ni and Pb. This behaviour is shown in Figure 7 for cadmium. The MSW leachates have had the largest increases, though the 8% IW leachates also have shown a small concentration rise. A rise in the concentration of leachate contaminants, particularly the heavy metals such as lead and cadmium, at the time of landfill stabilization is of concern for the planning of long term use of the landfill site. At this stage in the study there is no clear indication of whether the concentrations will continue to rise or will stabilize as the pH values stabilize. This stabilization phase is poorly understood and the test cells will be maintained to follow this activity.

The cause of the distinct differences in behaviour of leachate from MSW columns and 8%IW columns remains to be investigated. This difference is especially interesting in view of the dual behaviour of the 30%IW columns with two of the columns following MSW behaviour and two following 8%IW behaviour.

CONCLUSIONS

1. The modelling of leachate concentrations from the simulated MSW landfill test cells was not able to be extended to those containing industrial waste.
2. The differences in the leachate behaviour between MSW test cells and eight IW+MSW test cells may not be directly related to the industrial waste since two of the most heavily contaminated test cells (30%IW) had leachate concentrations not significantly different than the MSW leachates.
3. Six of the test cells containing industrial waste showed common behaviour patterns; more alkaline leachates after initially being acidic, less COD production, and lower concentrations of Ca, Mg, Mn, S, Zn, Cu, Ni, Pb, Co and Fe.
4. The test cells have shown an increase in concentration of Cd, Ni and Pb in the leachates in the past year and there has been a decline in biological activity during the same period.

REFERENCES

1. D.W. Kirk and M. Lau "Codisposal of Industrial and Municipal Wastes", Proceedings Technology Transfer Conference No.6, Part 3 Liquid and Solid Waste Research pp 209-244, 1985.
2. D.W. Kirk and S. Pirani "Comparison of Experimental Municipal Column Studies with Landfill Field Test Cells", Proceedings Technology Transfer Conference No.9, Liquid and Solid Waste Research, 1988.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support provided by the Ontario Ministry of the Environment and the technical support and encouragement provided by Mr. M.B. Fielding and Dr. J. Pimenta of the Ontario Ministry of the Environment.

TABLE 1

ANALYSIS OF THE INDUSTRIAL SOLID WASTE

Element	Fe	Zn	Ca	Mn	Pb	Cr	Al	Cu	Ni	Cd	Co
Weight Percent	26.8	14.1	11.9	4.01	1.99	0.21	0.21	0.18	0.04	0.04	0.003

The principal chemical species are in simple and complex oxide forms which include iron spinels and silicates.

Fig. 1 Zinc Concentration History
100% MSW

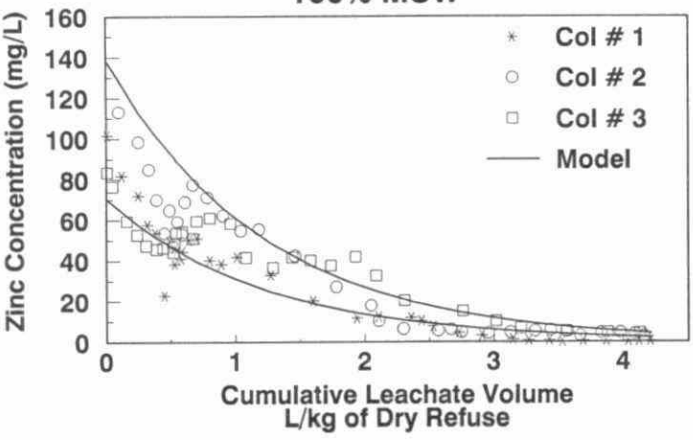


Fig. 2 Effect of Codisposal
MSW + 8% IW

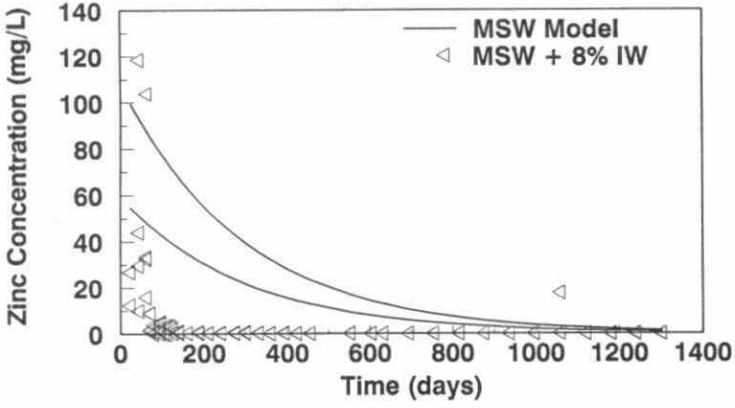


Fig. 3a Sodium Concentration History
100% MSW

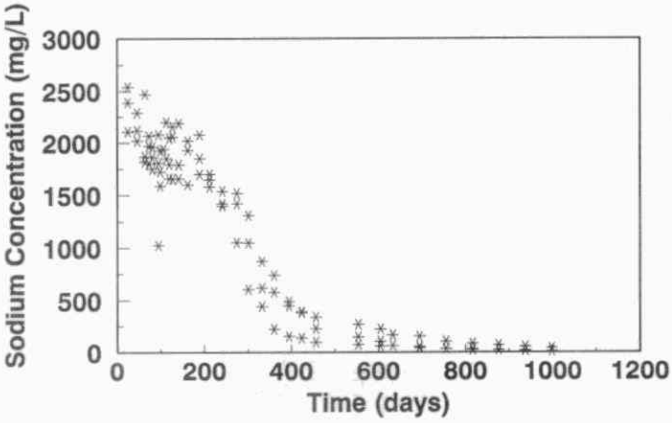


Fig. 3b Sodium Concentration History
MSW + 8% IW

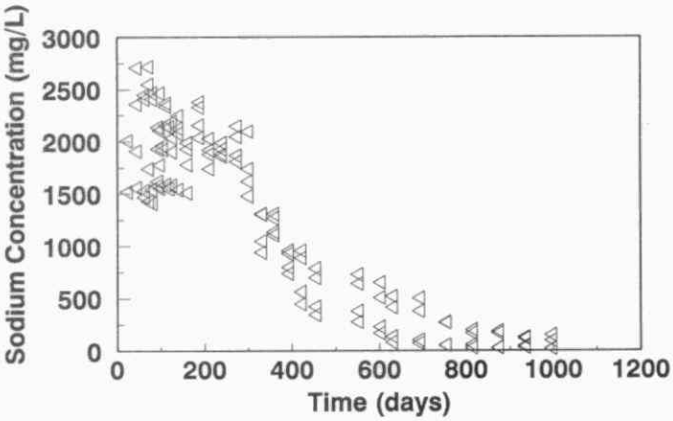


Fig. 4 Effect of Codisposal MSW + 30% IW

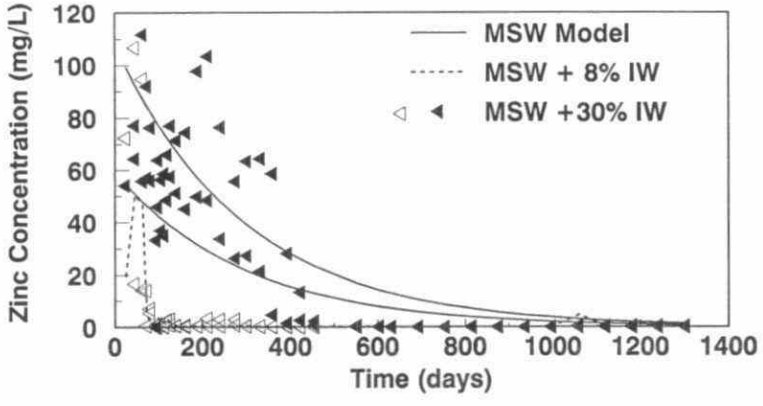


Fig. 5 Leachate pH

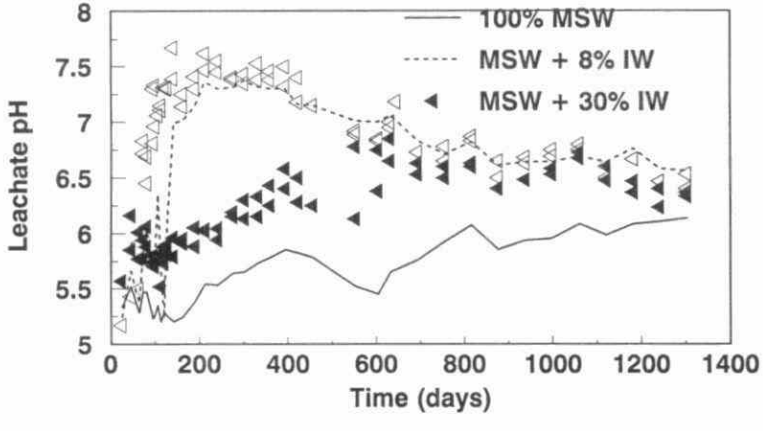


Fig. 6 COD Concentration History

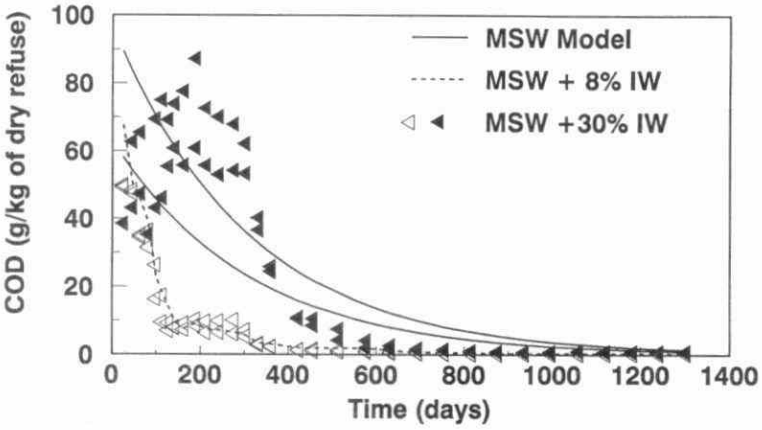
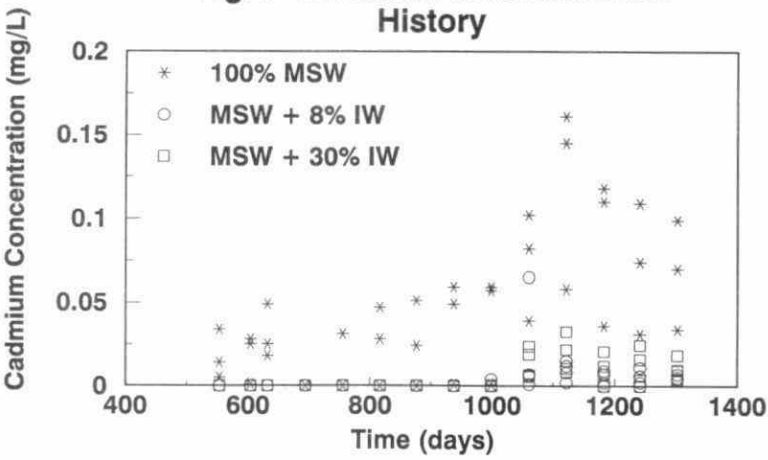


Fig. 7 Cadmium Concentration History



C6

MONITORING AND EVALUATION OF LANDFILL COVER LYSIMETERS

by:

K.J. McKague
Ecologistics Limited
Waterloo, Ontario

J.H. Cuthill
Department of Land Resource Science
University of Guelph
Guelph, Ontario

1.0 INTRODUCTION AND BACKGROUND

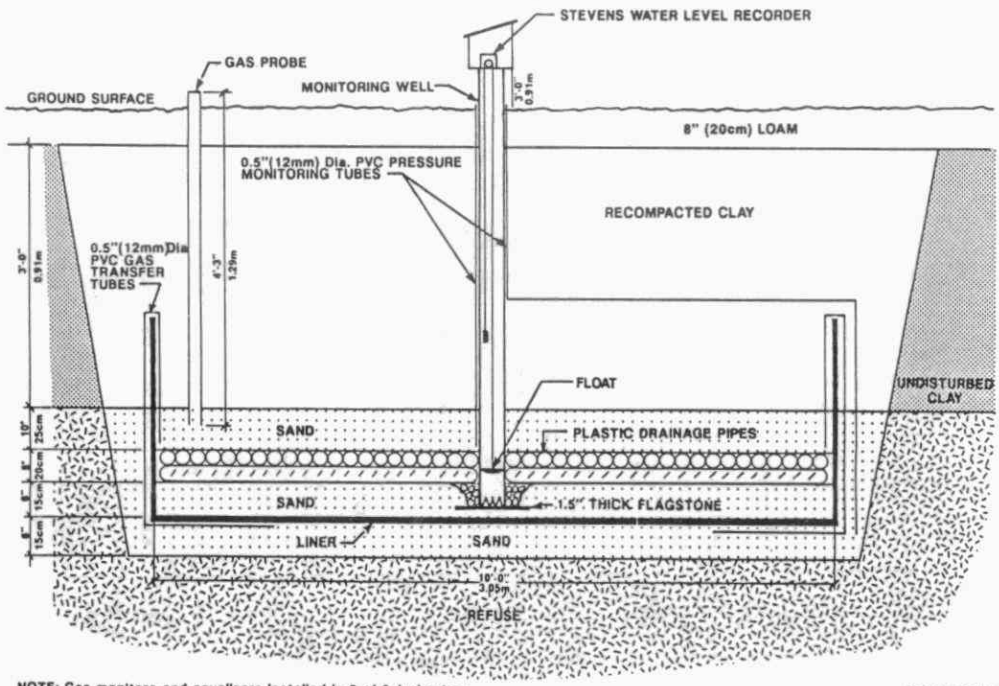
A soil cover or cap is the principal and often only barrier used to separate the underlying refuse from the elements, particularly precipitation, on a de-commissioned landfill site. Differing opinions exist as to what portion of leachate production can be attributed to infiltration of precipitation through landfill covers. Little is also known about the effect a cover's soil physical characteristics has on leachate production.

Environment Ontario has initiated a couple of studies aimed at developing a field-scale lysimeter that is capable of making repeatable and direct infiltration measurements through landfill covers. It is the monitoring and operation of the most recent set of 6 prototype landfill lysimeters which were installed on the Britannia Road landfill site in the summer 1987 that is discussed in this paper. Ecologistics Limited, in conjunction with personnel from the University of Guelph, were contracted to evaluate the effectiveness of these lysimeters as an infiltration measurement tool.

2.0 THE PROTOTYPE LYSIMETER

The typical cross-section presented in Figure 2.1 best illustrates the configuration of the lysimeters installed. Note that, while this base design was used for all six lysimeters, two different material mediums were tested for their applicability in the storage zone. A 21 cm deep storage zone consisting of a matrix of 100 mm diameter drainage tile was incorporated into three of the six lysimeters and is the storage zone type shown in Figure 2.1. The remaining three lysimeters utilized a 30 cm layer of washed gravel to form the storage medium. This added depth of storage zone was accommodated by reducing the thickness of the overlying sand layer. Calibration of the storage zones in each of the lysimeters indicated that the typical porosity of the storage zone in the "drain tile type" lysimeters was 91%, while the "gravel type" lysimeters possessed on average a porosity of 37%. Finally, note that while the cross-section indicates the presence of gas monitoring and exchange tubes in the lysimeter, only 2 of the six lysimeters had such installations incorporated during their construction.

FIGURE 2.1: Drain Tile Type Lysimeter Cross-Section



NOTE: Gas monitors and equalizers installed in 2 of 6 lysimeters

Not to scale

The theoretical operation of the lysimeter can be described briefly as follows. Rainfall or snowmelt not shed by the clay cap in the form of runoff, consumed by evaporation or stored in the loam cover or clay cap percolates through the cover system and is captured within the lysimeter's storage zone. As the storage zone fills with captured water, a Leopold-Stevens water level recorder documents the change in the stored water level. Calibration curves convert the change in stage to a volume. Serrated openings at the base of each of the lysimeters monitoring wells were incorporated to facilitate a rapid transfer of water between the monitoring well and the storage zone.

3.0 LYSIMETER RESPONSE TO PRECIPITATION

Upon completion of lysimeter installation, monitoring could commence. Initial monitoring of the lysimeters in the fall of 1987 and early winter of 1988 revealed that the lysimeters were not operating as expected. Water levels in the storage zones of all the lysimeters were fluctuating up and down considerably despite the fact that there were no leaks detected from the storage zone. An explanation of these well level observations was eventually obtained upon comparison of well level graphs with atmospheric pressure readings for equivalent time periods. Well level charts were found to be the inverse of the fluctuations graphed using the atmospheric pressure data. To overcome this difficulty, the lysimeters were "vented" by drilling numerous small holes into the side of the well casing within the region of the lysimeter's storage zone. This field modification was completed on all lysimeters by April, 1988. Following this modification, the lysimeter hydrographs possessed a shape that more closely matched that which would be expected for a filling storage zone.

In addition to venting the lysimeters, the study team also opted at the same time to install galvanized steel barriers upslope of three of the lysimeters as a long-term means of determining whether surface runoff from upslope and/or subsurface interlayer flow was contributing inputs to the lysimeters' storage zone. These barriers were installed vertically into the loam cover and extended into the clay cap. They were installed on an angle and for a length sufficient to allow any water flow encountering the obstruction to be diverted outside of the lysimeter area. Only lysimeters 1, 3 and 5 received this upslope barrier.

To assist in answering some of the questions concerning lysimeter configuration and the state of deterioration of the lysimeter materials, the Ministry of the Environment gave the study team approval to excavate one lysimeter of each storage type. Consequently only four (4) lysimeters remained for the full year analysis presented in this report. Upon excavation it was found that construction materials were still in good shape and that the thickness of the pertinent soil and storage layers were as indicated in the construction notes (within reasonable tolerances). Measurements from the flagstone to the bottom of the designated storage zones were also made on the drain tile type lysimeter. Data collected was used to locate pertinent layer locations for the remaining unexcavated lysimeters by making the assumption

that lysimeters having similar storage types were built identical to one another. Finally, at the time of excavation, the elevations of the bottom of the well of the remaining lysimeters, were determined, related to a permanent benchmark and documented for future reference.

A minimum of one (1) calendar year of data was considered necessary in order to observe and evaluate the lysimeter's operation through all four climatic seasons. Thus, once all field modifications had been made to improve and test lysimeter operation, both monitoring and analysis of results were possible. Observations of well hydrograph levels and precipitation made for the full year of monitoring are presented in Figures 3.1 through to 3.4.

4.0 INTERPRETATION OF LYSIMETER RESPONSE

A number of factors must be considered when interpreting the data presented in Figures 3.1 to 3.4. First, note that lysimeters 1 and 2 possess gravel storage zones which results in a more significant rise in water level for an equivalent change in volume stored than is displayed by the more porous drain tile storage zones of Figures 3.3 to 3.4. The presence of barriers placed upslope on lysimeters 1 and 3 need also be considered when interpreting the graphs. Related to this, as well, are the surface and subsurface depressions created by settlement in the vicinity of the lysimeter. These are just some of the factors that could influence water supply to the lysimeters. A summary of the different features associated with each lysimeter is presented in Table 4.1.

TABLE 4.1: MATRIX OF LYSIMETER FEATURES

FEATURE	1	2	3	4
Tile Storage Medium			*	*
Gravel Storage Medium	*	*		
Barriers	*		*	
Gas Vents		*	*	
Surface Depressions (cm)	7	10	10	4
Lysimeter Settlement (cm)	8	7	6	9

General trends in lysimeter response can be seen upon reviewing Figures 3.1 to 3.4. For the May - June period, infiltration leading to deep drainage was occurring at a relatively constant rate. The summer months of July, August and September saw very little deep drainage occurring. In the fall season, frequent precipitation resulted in increased deep-drainage, particularly in mid-November. During the winter months, very little deep drainage was observed due to frozen soil conditions. The April thaw, however, resulted in immediate and significant responses for all lysimeters with lysimeters 2 and 4 filling

Figure 3.1: Lysimeter #1 Well Hydrograph and Precipitation Data

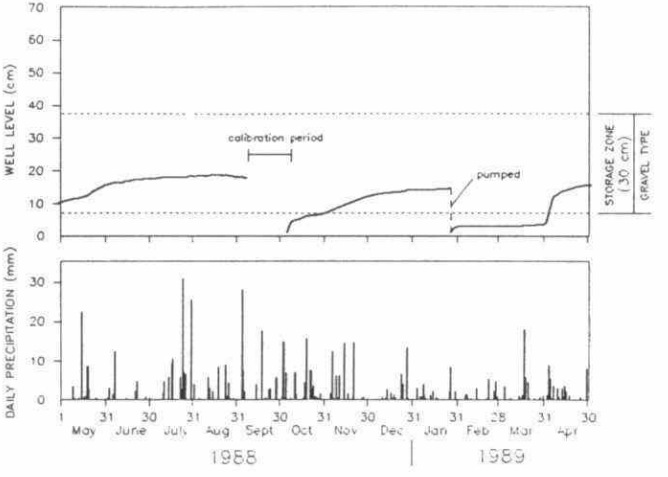


Figure 3.2: Lysimeter #2 Well Hydrograph and Precipitation Data

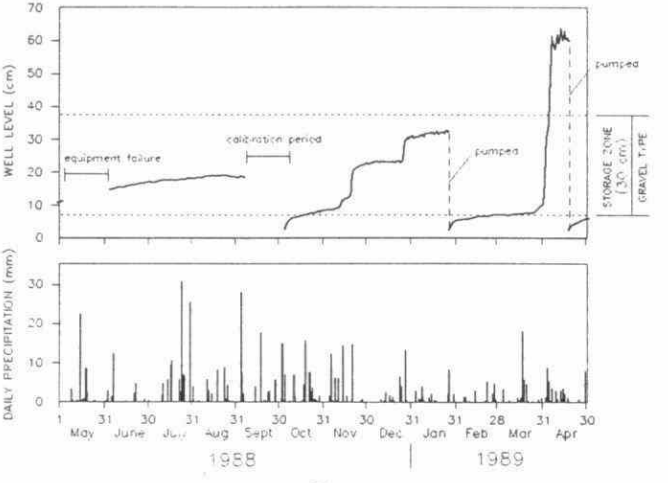


Figure 3.3: Lysimeter #3 Well Hydrograph and Precipitation Data

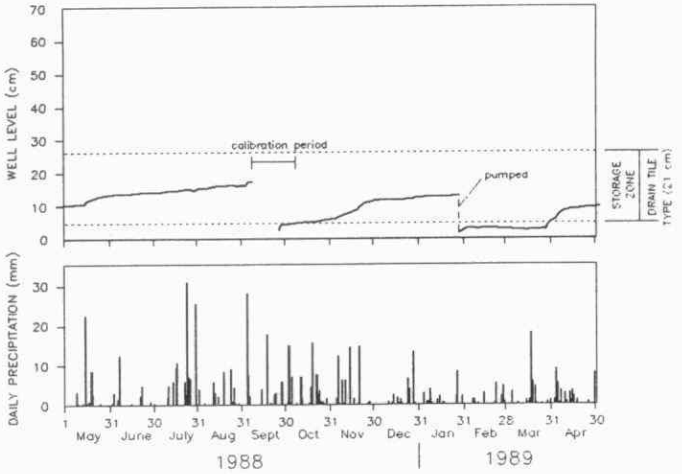
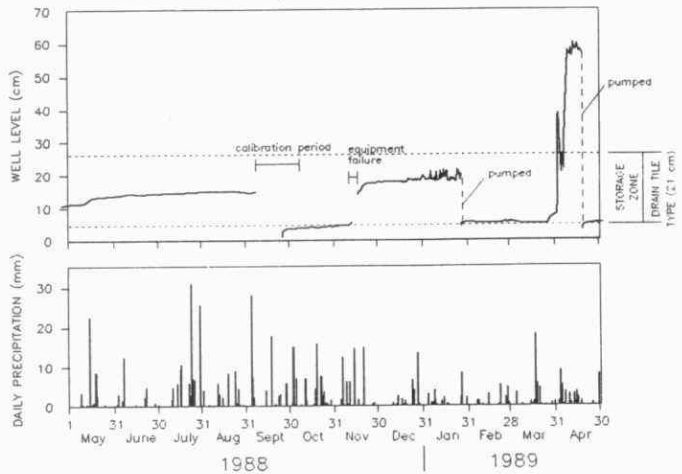


Figure 3.4: Lysimeter #4 Well Hydrograph and Precipitation Data



their storage zone in a matter of days. With the exception of the thaw, little correlation could be seen between individual precipitation events and hydrograph response. The dynamics of soil moisture and evapotranspiration rates were expected to be the factors contributing to this low correlation.

To analyze the collected data more thoroughly, the observations were partitioned into two month segments. A quantitative summary is presented in Table 4.2 showing the volume (equivalent depth) of deep drainage water collected by the 3 m by 3 m lysimeter along with the percent of total precipitation for the two month period which that volume of collected water represents. May - June data indicated that the lysimeters were collecting similar volumes of water with the exception of lysimeter 3. At the time the up-gradient barriers were installed, it was noticed that there was a depression or "bowl" over lysimeter 3 that was much more pronounced than that over the remaining lysimeters. Thus, a greater volume of precipitation could have been collected over lysimeter 3, giving the larger input response. Also present was a gas vent, installed independently of the lysimeter construction in the fall of 1987, which had a high potential of creating a preferential flow path.

TABLE: 4.2 SUMMARY OF LYSIMETER RESPONSE CURVE DATA

PERIOD	PRECIPITATION IN PERIOD (mm)	Percent of Precipitation mm of deep drainage			
		LYSIMETER NUMBER			
		1	2	3	4
May - June 1988	64.6	41.8% 27.0 mm	34.1% 22.0 mm	60.4% 39.0 mm	43.3% 27.97 mm
July - Aug. 1988	146.9	2.0 2.9	4.8 7.0	12.3 18.0	3.4 5.0
Sept. - Oct. 1988	138.0	5.8 8.0	5.8 8.0	16.1 22.3	1.6 2.21
Nov. - Dec. 1988	88.8	27.9 24.8	93.5 83.0	73.2 65.0	131.0 116.3
Jan. - Feb. 1989	44.9	7.2 3.23	32.6 14.4	7.2 3.23	26.7 11.98
March - April 1989	77.9	49.1 38.2	134.0 104.4	66.4 51.7	215.0 167.0
Totals (May '88 - April '89)	561.3 mm	18.5% 104.0 mm	42.5% 238.0 mm	35.5% 201.4 mm	59.0% 330.0 mm

July and August were abnormally hot and dry in 1988. Once again, the lysimeters all showed similar responses with the exception of lysimeter 3 where deep drainage continued very slowly in the first half of the period and again following the rainfalls of July 22 to 26. A likely explanation for this is a carryover of moisture from the previous period. With vegetative cover not fully established in the early summer of 1988, root penetration would not be deep enough to remove water from the deeper soil zones by evapotranspiration. Convenient flow paths to the storage zone, such as created by the gas vent, could contribute to giving a greater input to lysimeter 3.

Calibration of the lysimeters was undertaken in September and October 1988. Thus, data is incomplete for this time period. It would appear from the data available that lysimeter 3 was still receiving above normal inputs. Note as well that following pump-out of the storage zones the lysimeters displayed a relatively rapid rise in well level. This rapid rise was determined to be the consequence of the lag time required for water in the storage zone to recharge the well and reach a steady state.

The November and December responses were the first which clearly demonstrated the effect of barrier installation upslope from lysimeters 1 and 3. By late November, the area over lysimeter 3 had been regraded so that the ground surface elevation conformed with the surrounding area. Precipitation which fell in this time period seemed to give gradual responses with lysimeters 1 and 3 and very rapid responses with lysimeters 2 and 4. The difference in magnitude among these responses were quite large as well, as can be seen in Table 4.2. To obtain such a quick, voluminous input to a storage zone located under a layer of soil would require a continuous source of water available to act as a supply. Up-slope runoff water ponding on the surface could be such a source. This source could then be connected to the storage zone by means of a preferential flow path created either by soil cracks or the separation of the monitoring well or gas vent tube from the soil or surrounding bentonite sealant matrix.

While below freezing soil temperatures in January and February lowered infiltration rates significantly, data illustrated the trend of higher inputs being associated with the non-barriered lysimeters. With the lysimeter storage zones gradually being filled by January, fewer holes existed in the monitoring well to allow for rapid and efficient gas exchange between the storage zone and the atmosphere. Consequently, the barometric effect, encountered when the lysimeters were first monitored, was beginning to re-appear as can be seen by the fluctuations in the well water level hydrograph.

Three observations are prominent for the month of March and April. First, is the low level of infiltration during the first four weeks of March. Second, is the relative timing of the infiltration response, while third is the magnitude of the responses when they were recorded. Frozen soil conditions can account for the lack of infiltration for the month of March. It was not until March 24 through to the end of the first week of April that mean daily temperatures remained above the freezing point. This warming trend in the latter part of March resulted in similar responses initially from three of the four lysimeters as the landfill cap

thawed. In fact, the response of these three lysimeters appeared to be within hours of each other. The exception was lysimeter 1, where the presence of denser vegetation over the lysimeter would appear to have insulated the ground, thereby slowing the soil thawing process and delaying the response until April 3.

The magnitude of the responses, as well as the rate of response, are very revealing in this period. If preferential flow paths did not exist, it is extremely unlikely that the volume and rates of deep drainage recorded, particularly as seen for lysimeters 2 and 4 would be present when the physical characteristics of the soils comprising the landfill cap are considered.

5.0 CONCLUSIONS

Upon analysis of the lysimeter results, it was concluded that the lysimeters did not respond similarly to individual or monthly events. Even annual averages of infiltration were dissimilar ranging from 18 percent to 59 percent of the 12 month precipitation. The reasons for these dissimilarities can, to a large part, be attributed to the alterations made to some, but not all, the lysimeters during the project in an effort to obtain data which seemed reasonable. These changes, while necessary in order to understand the data being obtained and to make the lysimeters more operational, resulted in a group of lysimeters which each responded differently to precipitation inputs. Trends, however, among the more similar lysimeters were noticed (i.e. lysimeters 1 and 3 and lysimeters 2 and 4) as were trends during periods when infiltration levels were so low that the different modifications were not having an influence on the results. For instance, data indicates that lysimeters 2 and 4 both possessed some form of preferential flow path which conducted relatively large volumes of infiltration only when there was sufficient moisture to cause positive pressure. This is reflected in the data of the monitoring period of November to December and again in March to April. Arguments can be made that these preferential flow-paths are a natural consequence of desiccation and stress cracks which develop on soil covers. Having considered all factors, however, the researchers concluded that the preferential flow paths were far more likely to be a consequence of the presence of the lysimeter, rather than an effect of variations in landfill cap characteristics and deterioration.

The fact is that the lysimeters did not respond similarly to precipitation events in either the short term or long term. This in part is a result of the alterations, especially the installation of up-slope barriers, made during the study. Observations made while the alterations were in place have, however, enable a better understanding of the factors affecting lysimeter operation. With this knowledge, measures to correct the problems encountered could be incorporated into future lysimeter designs.

6.0 RECOMMENDATIONS FOR FUTURE LYSIMETER INSTALLATIONS

Knowledge of where the water originates that enters the lysimeters storage zone is not deemed necessary for purposes of this study. Of interest is only the capability to collect that portion of water which eventually passes through a "typical" 3 m by 3 m section of landfill cover. The key then, for collecting such data, is to install a lysimeter which can be built and act as closely as possible as the surrounding cover and garbage system while enabling accurate data collection. The following minor modifications to the previously described design and data collection methods were recommended:

1) Vent the lysimeter monitoring wells within the storage zone area prior to their installation. This will ensure efficient air/gas exchange improving data collection results.

2) Make the storage zone more sensitive by reducing zone porosity or alternatively measure inputs volumetrically, on a monthly basis, using the water level recorder to determine times of inputs only. Difficulties in calibration would be overcome in implementing the first option. Improved accuracy of results would be a consequence of either of these changes.

3) Follow a more precise protocol for lysimeter installation to ensure the landfill cover over the lysimeter matches, as close as possible, the surrounding area.

4) Address all components of the lysimeter design which could create potential for preferential flow paths. Deflection collars or "skirts" at strategic points around the circumference of the monitoring well, as well as liberal use of bentonite around the perimeter of the lysimeter are recommended.

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C7

The Effect of Wellbore Dilution on the Results of Tracer Experiments Conducted in Fractured Rocks

Kentner S. Novakowski
and
John A. Cherry

Waterloo Center for Groundwater
Research, University of Waterloo
Waterloo, Ontario, N2L 3G1

Introduction

Many landfills and industrial sites in North America are situated such that chemical leachates emanating from these facilities are contaminating groundwater in underlying bedrock. Examples of this can be found in Southern Ontario where the underlying materials consist of a thin veneer of overburden overtop moderately to highly fractured shale of Ordovician age.

At the current time, assessment of groundwater velocity in these fractures and thus the prediction of the rate of leachate migration, is based on a conceptual model known as the parallel-plate model. Unfortunately, the parallel-plate model has been shown to have numerous flaws when used in this regard (Novakowski, et al., 1988). Thus to more accurately predict contaminant migration in fractured rock, an evaluation of all existing conceptual models is required and a new conceptual model developed. Experimentally, the most appropriate technique with which to do this is using the results of a well controlled tracer experiment conducted under natural groundwater flow conditions.

During a natural gradient tracer experiment, water stored in a monitoring well will dilute the concentration of tracer entering the well such that the changes in concentration measured in the well are delayed relative to the changes in concentration in the formation. This problem has been recognized for mass transport problems in porous media and a theoretical study has been conducted (Palmer, 1988). In addition, several recent analytical models used for analyzing the results of advective tracer experiments, have included the wellbore mixing effect during the problem formulation (Hodgkinson and Lever, 1983; Moench, 1989). None of these studies however, have focussed on the nature of the problem in the context of mass transport in fractured rock.

Consequently, in preparation for a natural gradient tracer experiment to be carried out in the Georgian Bay Shale, a theoretical and laboratory study was conducted of wellbore dilution in monitoring wells completed in fractured rocks. The objective of the study is to develop mathematical methods and experimental techniques with which to improve the accuracy of concentration measurements obtained during tracer experiments. The study is conducted using the results of several laboratory tracer experiments carried out in an artificial fracture. The results are analysed using a mathematical model developed to properly account for the mixing conditions in a monitoring well.

Mathematical Development

Mass transport under uniform and steady groundwater flow conditions is described by the following linear partial differential equation (in dimensionless form)

$$\frac{\partial C_D}{\partial t_D} + \frac{\partial C_D}{\partial x_D} = \frac{\partial^2 C_D}{\partial x^2_D} \qquad [1]$$

where C_D is dimensionless concentration, C/C_o (C_o is the initial concentration), t_D is dimensionless time, $\bar{v}^2 t/D$ ($\bar{v}$ is groundwater velocity and D is the coefficient of hydrodynamic dispersion), and X_D is dimensionless distance, $X\bar{v}/D$.

To use equation [1] for simulating the results of tracer experiments, an appropriate inner boundary condition must be stipulated. Assuming that equation [1] represents flux-averaged concentration (Van Genuchten and Parker, 1984), a first-type boundary condition can be employed to simulate a well mixed reservoir (or well) contacting the flow domain. In mathematical terms, this is given by:

$$C_D(0,t_D) = 1 \qquad [2]$$

There are numerous alternatives to equation [2], some of which can account for instantaneous mixing within a finite-volume reservoir. However, because the tracer experiments conducted for this study were completed in a fashion such that equation [2] best describes the inner boundary condition, further development of the analytical model is conducted using [2] as the only inner b.c. It should be noted that solutions to equation [1] in consideration of other possible b.c. have been obtained but will not be reported here.

The outer boundary condition which describes mixing in the well can be formulated in two ways. One method, which includes a continuity condition at the exit boundary, leads to an unrealistic physical condition near the exit boundary and will not be considered here. The other method does not require a continuity condition and thus conserves mass. This condition is given by

$$\beta_{DO} \frac{dC_{DW}(t_D)}{dt_D} = C_D(P,t_D) - C_{DW}(t) \qquad [3]$$

and is found using application of the local flux-averaged transformation:

$$C_D = C_{DR} \Big|_{X_D = P} - \partial C_{DR} / \partial X_D \Big|_{X_D = P} \qquad [4]$$

The concentration, C_{DW}, is the concentration measured in the well and β_{DO} is the wellbore mixing coefficient equal to the volume of the well times the groundwater velocity divided by the cross-sectional area available for flow times D. the coefficient P is known as the Peclet number and equals $\bar{v}L/D$ where L is the length of the flow domain. Equation [3] was also found by Palmer (1988) using a less rigouous mathematical argument.

The initial conditions for equations [1] and [3] are respectively:

$$C_D(X_D, 0) = 0 \qquad [5]$$

$$C_{DW}(0) = 0 \qquad [6]$$

and the solution to [1] - [6] is easily obtained using the Laplace transform method. The solution in the Laplace domain for the concentration in the well, C_{DW}, is

$$C_{DW}(p) = \frac{1}{p\,(\beta_{DO}\,p + 1)} \exp\left\{ \xi P \right\} \qquad [7]$$

where p is the Laplace variable and ξ is equal to $1/2 - \sqrt{(1/4+p)}$. Because equation [7] is an irrational function of p, the analytical inversion of [7] will lead to an integral of exp which will be difficult to evaluate. Therefore, real space values of C_{DW} are obtained using a numerical inversion algorithim (Talbot, 1979).

Experimental Method

As a means of evaluating the apparatus used to obtain tracer concentrations in a monitoring well, several tracer experiments were conducted in an artificial fracture. The fracture was manufactured of two 1.2 m x 1.2 m acrylic plates about 9.5 mm in thickness. These plates are oriented horizontally and separated by 15-20 machinists shims, 0.75 mm thick, distributed about the area of the fracture. The fracture plane was sealed along two parallel sides and mixing boxes, several litres in volume, were constructed at each end. An acrylic tube (75 mm in diameter) was constructed to pass through the center of the plane in a perpendicular fashion, thus simulating a borehole. Two electrode ports were placed within the plane so that the actual concentration of the tracer flowing in the fracture could be determined directly.

The tracer experiments were conducted by establishing a steady-flow field between the mixing boxes. Hydraulic gradients were maintained using a system of mariotte bottles. Tracer (the anion Br^-) was introduced as a step-function into the source mixing box and concentration was monitored in the borehole. A red dye was also added to the tracer solution to visualize the flow processes.

The intersection of the fracture in the borehole was isolated using a set of pneumatically-inflated straddle-packers. The packers were designed and manufactured specifically for the purpose of the natural gradient tracer experient. For the initial laboratory experiments, the packers were separated by about 0.10 m giving an interval volume of about 0.36 L. Concentration was measured in the isolated interval by recirculating the interval water through a flow cell containing an ion specific electrode. This configuration and technique was initially planned to be employed in the field experiment. For the later laboratory experiments, the interval

volume was reduced to about 0.025 L to assess the influence of the size of the isolated volume on the test results. This was achieved by reducing the packer spacing to 0.015 m and filling the open space with a PVC plug ported to allow the recirculation of water.

Results and Discussion

A total of 14 experiments were conducted, 12 using the large-volume apparatus and 2 using the reduced-volume system. Several of the initial experiments were conducted without active recirculation or sampling so as to obtain undisturbed measurements of concentration from the electrode ports in the fracture plane. The results from these experiments were analysed using the first type b.c. solution of Ogata-Banks (assume a flux-averaged concentration). The results from the balance of the experiments were obtained from the recirculated fluid in the borehole and analysed using equation [7].

Based on visualization of the flow it was observed that most of the tracer was transported along a channel about 0.30 m wide and 1.4 m long, transversely oriented in the fracture plane. The results of the experiments were analysed using these dimensions as well as the dimensions of the entire plane.

Table 1. Calculated aperture and velocity where the channel dimensions are employed.

Exp.	ΔH (m)	Q (m^3/s)	2b (m)	$\bar{v}$ (m/s)
4	0.0495	3.233-06	0.000721	0.01494
5	0.0330	2.183E-06	0.000724	0.04004
7	0.0105	1.303E-06	0.000893	0.00486
8	0.0296	1.027E-06	0.000584	0.00585
9	0.0310	1.200E-06	0.000605	0.00659
10	0.0373	1.800E-06	0.000652	0.00659
12	0.0142	1.467E-06	0.000841	0.00581
13	0.0100	1.667E-06	0.000989	0.00562
14	0.0096	1.453E-06	0.000856	0.00507

Table 2. Calculated aperture and velocity where the dimensions of the fracture plane are employed.

Exp.	Δ H (m)	Q (m^3/s)	2b (m)	$\bar{v}$ (m/s)
4	0.0495	3.233E-06	0.000431	0.00624
5	0.0330	2.183E-06	0.000433	0.00420
7	0.0105	1.303E-06	0.000534	0.00203
8	0.0296	1.027E-06	0.000349	0.00245
9	0.0310	1.200E-06	0.000362	0.00275
10	0.0373	1.800E-06	0.000390	0.00384
12	0.0142	1.467E-06	0.000503	0.00243
13	0.0100	1.667E-06	0.000591	0.00235
14	0.0096	1.453E-06	0.000572	0.00212

Table 1 and 2 show the apertures (2b) and velocities ($\bar{v}$) calculated from the hydraulic properties of the fracture. The standard form of the cubic law (parallel-plate model) was used to calculate these values. Table 1 shows the results where the channel dimensions (1.4 m x 0.30 m) are used and Table 2 shows the results where the full fracture dimensions are used.

Comparing the apertures between Table 1 and Table 2, it is evident that the dimensions of the channel are best employed when analysing the data from the tracer experiments. The average 2b calculated using these dimensions is about 774 μm, in good agreement with the expected value (the thickness of the machinist's shims). The average 2b calculated using the full dimensions of the plane is 463 μm, which is only 2/3 the expected value.

To determine the hydrodynamic dispersion coefficient, model fits were made to the concentration data obtained from the electrode ports and from the borehole. The fits were made by eye, adjusting the velocity $\bar{v}$ and the longitudinal dispersivity, α_L ($\alpha_L = D/\bar{v}$).

Table 3 shows the dispersivities and Peclet numbers for 7 of the experiments. These values are determined from the data obtained from the electrode ports and should reflect the dispersive characteristics of the fracture. The average P and α_L are 122 and 0.36 m, respectively. However, due to the large variation in dispersivity measurements, it is assumed that these results are influenced to an unknown degree by mixing around the electrode ports. The α_L predicted using the parallel-plate model (Taylorian dispersion theory) is about 0.08 - 0.01 m using example velocities typical of the experimental conditions. This is somewhat larger than the values determined using the model fits and suggests that despite possible mixing effects, the values determined using the data obtained from the electrode ports reasonably represent the dispersive characteristics of the artificial fracture.

Table 3. Results of the simulations of the data obtained from the electrode ports.

Exp.	Peclet Number	Dispersivity (m)
4	68.1	0.020
5	100.4	0.013
7	136.4	0.010
8	266.1	0.005
9	220.6	0.006
10	137.8	0.010
12	129.3	0.010

Table 4 shows the results of the modelling using equation [7] as applied to the data obtained from the recirculating borehole fluid for experiments 8,10,13 and 14. Experiments 8 and 10 were conducted using the large-volume interval and 13 and 14 were conducted using the smaller-volume interval. In comparison with Table 3, is is clear that even when accounting for mixing in the test interval (i.e. equation [7]) other processes act to increase the apparent dispersion as measured in the borehole. This is evidenced by the one order of

magnitude diffference between the results obtained from the electrode ports and those obtained from the borehole. However, a sensitivity analysis using equation [7] has shown that when the mixing coefficient is large, as with experiments 8 and 10, the sensitivity of the model curve to changes in α_L is very small. Thus the reliability of the P determined from experiments 8 and 10 may be somewhat poorer than for experiments 13 and 14.

Table 4. Results of the simulations of the data obtained from the borehole during experiments 8, 10, 13 and 14.

Exp.	Dispersivity (m)	Peclet Number
8	0.017	36.0
10	0.020	29.4
13	0.100	6.0
14	0.046	12.9

The largest possible influence on dispersion within the wellbore is likely the mixing process itself. This is suggested when the results for experiment 8 and 10 are compared to 13 and 14. A substantial decrease in the value of the Peclet number is observed for experiments 13 and 14. Visualization of the flow during experiments 13 and 14 showed a substantial increase in the divergence of the streamlines near the wellbore relative to previous experiments. This may have resulted in flow separation and stagnation near the wellbore-fracture interface causing increased dispersive flux into the wellbore. This finding is important because it suggests that the one-dimensional mass transport equation will not suffice when used to simulate the two-dimensional dispersive effects around a wellbore. Furthermore, it appears that modifications of the test interval size as a means of increasing the reliability of the α_L measurement, will need to be conducted in consideration of these extraneous 2-D effects.

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C8

Landfill Leachate Recirculation: Effects on Plant Vigour Leachate Quality and Clay Surface Infiltration. Part I: Plant Vigour.

P.M. Cureton*, P.H.Groenevelt and R.A. McBride,
Department of Land Resource Science
University of Guelph, Guelph, Ontario N1H 2W1

1. INTRODUCTION

Recirculating municipal solid waste (MSW) sanitary landfill leachate through a vegetated clay surface liner and through the refuse cell may offer an alternative approach to the management of these wastewaters. It is proposed that recirculation may afford benefits which include lowered volume of leachate, improved rate of refuse decomposition in the cell, and attenuation of organic and inorganic leachate constituents in a soil environment. The benefits of a fully contained landfill where biological, chemical, and physical renovation processes may be improved due to the added moisture from recirculation means that the landfill may become less of a threat to groundwater and surface water quality sooner (Pohland, 1980; Barber and Maris,1984). Indeed, pioneers of this idea envisioned recirculation as a means of leachate storage,of primary treatment to reduce contaminant strength, and of increased biological stabilization of waste at the acid fermentation and the methane fermentation stages of organic molecule decomposition (Pohland,1980; Tittlebaum, 1982; Barber and Maris, 1984; Lee et al.,1986; Pohland and Gould, 1986).

In previous experiments leachate has been recirculated beneath the cell's top soil cover and directly into the refuse (Pohland,1975). Barber and Maris (1984) hypothesized, however,that recirculation to a vegetated surface could increase the rate of stabilization as well as decrease overall volume of leachate by evaporation from the soil surface and by plant

transpiration.

The desirable quality endpoint of the recirculated leachate is one whereby the leachate could meet either provincial stream and lake water quality guidelines or municipal sewer by-law concentration limits.

2. OBJECTIVES

This experiment set out to determine the effects of continuous leachate recirculation to a vegetated clay liner on the:

1. Soil water budget with cover crops of 4 plant species.
2. Vigour/health of vegetation.
3. Change in quality of 2 disparate landfill leachates.
4. Infiltration rate through a clay surface liner.

This paper will discuss results of the soil water budget and plant vigour aspects (objectives 1 and 2).

3. MATERIALS AND METHODS

3.1 Simulated Landfill Design and Recirculation Treatments

Thirty nine (39) in-ground, bottom-draining lysimeters at the University of Guelph were filled to simulate a landfill profile. The lysimeter nest was rainsheltered. Each lysimeter was roughly 1.3 m in depth and 1.0 m in diameter. The sequence of layers beginning at the bottom was i) a geotextile-lined drainage bed of gravel overlain by sand ii) 35 cm deep layer of sandy soil which had been contaminated by landfill leachate at the Muskoka Lakes site (representing a homogeneous, highly decomposed refuse layer) and iii) a 50 cm thick surface liner of natural clay soil from the Glanbrook landfill in the Regional Municipality of Hamilton-Wentworth. Each lysimeter drained individually through polypropylene tubing to individual containers in an underground bunker. Effluent collected from the drains was sampled bi-weekly and tested for pH, chemical oxygen demand (COD),

electrical conductivity (EC), chloride, metals (Zn, Ni, Cr, Cd) and volatile organics. Similarly, samples were taken bi-weekly from the irrigant containers. At a depth of 30 cm in the clay layer, soil solution samplers were installed to track the movement of leachate constituents.

3.2 Plant Species

Vegetation treatments included two woody species (Salix babylonica and Populus spp. NM6), hereafter referred to as willow and poplar, respectively. Two grass species (Phalaris arundinacea L. and Alopecurus praetensis L.) were also established on some of the lysimeters hereafter labelled reed canarygrass and meadow foxtail, respectively. These species were selected on the criteria of high water requirements, tolerance to wet soil conditions, short establishment period, Leaf Area Index, degree of ground cover (erosion control), winter hardiness and reseeding potential. Plants were established in the spring of 1988, the grasses from seed, the poplar as cuttings and the willow as seedlings. After one month of water irrigation during establishment, the leachate applications began and continued 5 days/week for 13 weeks in 1988. Early in the 1989 field season, all plants were water irrigated to ensure plant survival. Leachate irrigation recommenced July 7, 1989. The data presented in this paper are from the second irrigation season in 1989.

3.3 Leachate Sources

The two sources of untreated leachate were the Township of Muskoka Lakes and the City of Guelph municipal solid waste sanitary landfill sites. Leachate was collected from each landfill site in May, 1989 (the beginning of the second season) and stored in 200 l containers. Aliquots pumped with a barrel pump were delivered to the surface of lysimeters as the irrigant.

Effluent collected at the lysimeter drains was returned to the corresponding holding tank, thereby creating 39 individual, continuously recirculating systems. Three groups of leachate constituents of interest were plant macronutrients (N,P,K), metals (Zn, Ni, Cr, Cd) and volatile organics (trichloroethylene and substituted aromatics: benzene, toluene and xylene).

The experiment was designed as a factorial (3 replications) with 3 irrigant types (water control, Guelph leachate and Muskoka leachate), 4 plant species and an unvegetated surface. Since only 39 lysimeters were available, the full 3x5x3 factorial was not possible. The control treatments and treatments using the stronger Guelph leachate were deemed of more interest. Hence, there were no woody species (poplar and willow) irrigated with Muskoka leachate.

4. RESULTS AND DISCUSSION

4.1 Evapotranspiration

The amount of actual evapotranspiration (AE) is usually proportional to biomass production and is a good indicator of plant vigour. Plant species with high water requirements would be desirable in a recirculation system where it is important to reduce the volume of leachate that needs to be handled.

The AE was calculated for all treatments according to:

$$AE = IRR - EFF - STORAGE$$

where:
- AE = actual evapotranspiration (mm)
- IRR = irrigant added (mm)
- EFF = effluent collected (mm)
- STORAGE = change in moisture content of soil (mm)

Leachate was applied twice weekly for 8 weeks in 1989. As expected,

both tree species evapotranspired more than either of the grass species. Water-irrigated poplars used the most liquid (64.23 $mm.wk^{-1}$) vs. the 58.0 $mm.wk^{-1}$ used by leachate fed poplars (Fig. 1). More interesting is the fact that willows irrigated with Guelph leachate used more liquid (62.93 $mm.wk^{-1}$) than the willow water controls (60.05 $mm.wk^{-1}$). This occurred despite the fact that, during the last 3 weeks of irrigation, the Guelph leachate-irrigated trees were showing signs of stress(i.e. premature senescence). In a conventional leachate recirculation system where rainfall is not excluded, willows may still be a possible choice as a cover species if leachate is alternated with or diluted by natural rainfall.

The most encouraging result was that during this time reed canarygrass used 53.44 $mm.wk^{-1}$ of Guelph leachate, or roughly the same level of consumption as exhibited by the trees, whereas the control swards and those irrigated with Muskoka leachate consumed only 27.53 $mm.wk^{-1}$ and 29.45 $mm.wk^{-1}$, respectively. Perhaps more importantly, the reed canarygrass irrigated with leachate did not show any phytotoxicity symptoms. Meadow foxtail plants consumed an average of 28.63 $mm.wk^{-1}$ of liquid regardless of the type of liquid applied.

4.2 Foliar Biomass

An analysis of variance indicated that after 17 applications, there was significantly higher dry foliar biomass accumulation ($p < 0.05$) for Guelph leachate-irrigated reed canarygrass (0.764 $kg.m^{-2}$) than for either the Muskoka leachate-irrigated plots (0.367 $kg.m^{-2}$) or the water-irrigated control (0.220 $kg.m^{-2}$) (Table 1). Meadow foxtail irrigated with both of the landfill leachates resulted in significantly higher ($p < 0.05$) live foliar biomass accumulation (0.523 and 0.341 $kg.m^{-2}$ for Guelph and Muskoka

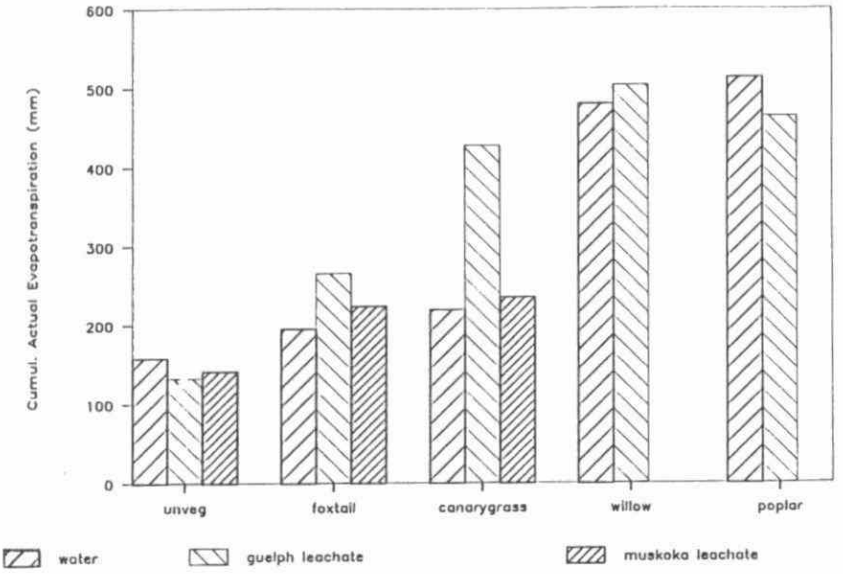

Fig. 1 Cumulative actual evapotranspiration (mm) July 7 - Sept. 12, 1989.

leachate, respectively) than in the water control plants (0.128 $kg.m^{-2}$). The response of the trees was dramatically different from that of the grass species. Whereas the grasses thrived on both of the leachates applied, full leaf senescence had occurred in the trees with leachate applied by the end of 17 applications. An analysis of senescing poplar and willow leaves was performed at the Forest Insect and Disease Survey Unit of the Canadian Forestry Service which concluded that the leaf damage was primarily a result of an abiotic agent (i.e.leachate). The symptoms observed were characteristic of vegetation exposed to drought. This supports the hypothesis that the high measured electrical conductivity of the Guelph leachate (average 7.85 $mS.cm^{-1}$) results in a significant osmotic potential component in the total water potential of the soil solution (calculated as approx. -282.6 kPa). This can create similar symptoms in plants as those growing in dry soils. Since there were no live leaves remaining on the Guelph leachate irrigated trees at the end of the irrigation schedule, the t-test on live foliar biomass indicated that after 17 applications leachate-irrigated poplar and willows had significantly lower mean live leaf biomass than their water control counterparts. The dry biomass of poplar trees irrigated with water was 0.676 $kg.m^{-2}$ as compared to 0.005 $kg.m^{-2}$ for Guelph leachate-irrigated poplars. Willow dry foliar biomass was 0.285 $kg.m^{-2}$ and 0.0 $kg.m^{-2}$ for the water and leachate-irrigated treatments, respectively.

Table 1. Mean dry foliar biomass ($kg.m^{-2}$) after 17 applications

Liquid Applied	Species			
	Reed canarygrass	Meadow foxtail	Hybrid poplar	Weeping willow
Water Control	0.222[a]	0.128[a]	0.676[a]	0.285[a]
Muskoka leachate	0.367[a]	0.341[b]	-	-
Guelph leachate	0.765[b]	0.523[b]	0.005[b]	0.0[b]

Note: Means in a column with the same letter are not significantly different at the 0.05 probability level.

A second measure of vegetation vigour was the height growth attained during the irrigation season. The results for the uncropped (first growth) grasses supported the results found from foliar biomass. Reed canarygrass attained a significantly greater maximum height growth when irrigated with Guelph leachate (91.0 cm) than with Muskoka leachate (67.3 cm) (Table 2),which in turn was significantly greater than the water irrigated control plants (48.7 cm, Pr>F = 0.0001). The meadow foxtail height growth results were comparable. Both the Guelph and Muskoka leachate-irrigated plants attained significantly greater maximum height growth (73.3 cm and 67.0 cm, respectively) than the water control plants (49.3 cm, Pr>F = 0.019).

Tree height growth during the irrigation season in 1989 was highest for Guelph leachate-irrigated poplars (107.9 cm) and significantly different (Pr>F = 0.023) from the 75.9 cm height growth of the water-irrigated poplars. Similarly, willows irrigated with Guelph leachate attained greater height growth (63.9 cm) than the water control willows (26.5 cm, Pr>F = 0.0001).

Table 2. Mean height growth (cm) during application.

Liquid Applied	Species			
	Reed canarygrass	Meadow foxtail	Hybrid Poplar	Weeping Willow
Water (control)	48.7[a]	49.3[a]	75.9[a]	26.5[a]
Muskoka leachate	67.3[b]	67.0[b]	-	-
Guelph leachate	91.0[c]	73.3[b]	107.9[b]	63.9[b]

Note: Means in a column with the same letter are not significantly different at the 0.05 probability level.

5. CONCLUSIONS

Of the 4 species tested, reed canarygrass outperformed the others in most of the test results and seems to offer the greatest potential as a landfill cover species under a continuous landfill leachate recirculation system. It has a high water requirement, using up to 7.63 $mm.day^{-1}$ in the summer season, even when the electrical conductivity of the applied liquid is as high as 13.5 $mS.cm^{-1}$. The accumulated biomass from one cutting (June 5-Sept 5, 1989) was 0.765 $kg.m^{-2}$. The leachate-irrigated grass swards outperformed the water control swards in terms of both biomass production and height gain. There was no indication of disease or drought in the grasses, particularly in the reed canarygrass, as there was in the leachate-irrigated poplar and willow.

6. ONGOING RESEARCH

Data analysis continues on the 1989 measures of field saturated hydraulic conductivity, K_{fs}, of the clay surface liner. Samples of the

lysimeter effluent and soil solution at 30 cm are undergoing analysis for plant nutrients (N,P,K) and metals (Zn, Ni, Cr, Cd).

Samples of both irrigants and effluents gas been analysed for volatile organics at the Canada Centre for Inland Waters, Burlington, Ontario. These data are presented in part by Lesage et al. in an adjunct paper.

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C9

DEGRADATION OF ORGANIC SOLVENTS IN LANDFILL LEACHATE.

Suzanne Lesage, National Water Research Institute, Environment Canada, Burlington.
Peter Riemann and Raymond McBride, University of Guelph

INTRODUCTION

The purpose of the study was to document the degradation pathways of organic solvents present in landfill leachate stored in holding tanks , and to look at the possible impact to the underlying ground water, of organic contaminants present in landfill leachate applied to land by spray irrigation. Kaplan et al. (1987) showed that both the pH and redox potential of wastewater change dramatically with depth in wastewater stabilization ponds, with intense anaerobic reducing conditions existing at dephts below 1m. The holding tanks were used as a model of the landfill leachate holding lagoons. Anaerobic reducing conditions also often prevail in contaminated ground waters (Champ et al. 1979) and therefore it was postulated that degradation of contaminants in the landfill leachate would follow the same pathways that are prevalent in anoxic ground waters.

Municipal landfill leachates were collected from two sites known to have distinctly different contaminant composition: the Muskokas and Guelph. The leachate was stored in 45 gallon holding tanks at ambient temperature for several months. Leachate was removed periodically to irrigate a series of lysimeters and analysed for volatile compounds on the Ontario MISA list of priority chemicals. In the first year of the study the disappearance of chemicals was followed over a period of four months.

In the second year of study, fresh leachate was obtained and the compound Freon-113 which was not found originally in either of the leachates was added and its degradation was followed. This was of interest since there has been evidence of biodegradation of this heretofore recalcitrant compound in groundwater (Lesage & al. 1989). Freon-113 is used as a refrigerant and as a degreasing agent in the electronic sector and is a common groundwater contaminant in Silicon Valley (Harding Lawson Associates, 1987). It is one of the compounds that are currently thought to be contributing to the depletion of the ozone layer.

SAMPLING

The leachate was stored in individual 200 L holding tanks kept in a three-feet-deep pit in the ground surrounded by peat moss, which provided insulation. Sampling was done by lowering into the holding tanks at least two feet below surface, 25 mL glass vials held in a wire basket made to fit the vials . The vials were sealed with teflon-coated disks ensuring that no airspace was trapped, refrigerated immediately and transported to the laboratory for analysis.

The leachate was used to irrigate a series of lysimeters which were vegetated with grass and wood species. Effluents were collected as described above.

ANALYSIS

The analysis for volatile organic compounds was conducted within two weeks of sampling. Because of the expected high level of contamination, 1-2 mL aliquots were used for analyses and diluted to 10 mLs with uncontaminated groundwater. The analysis was conducted on a Unacon-810 purge and trap concentrator directly interfaced to a Hewlett-Packard model 5970 GC-MSD. The analytical column was a J&W DB-624 fused silica capillary column, 30 m in length, 0.32 mm i.d., 1 um film thickness. The GC was cooled to -15°C with CO_2 and ramped to 130°C at 10°/min. Chlorobenzene-d5 and difluorobenzene were used as internal standards. Standards solutions were prepared from the purest available chemicals.

RESULTS

1st Year of the study

The results that were obtained on Guelph landfill leachate which was used as irrigant in the study are listed in Table 1. There contaminants were both chlorinated solvents and aromatic hydrocarbons.

Several months later,(Table 2) it was apparent that most of the chlorinated compounds had disappeared in the irrigant holding tanks. This disappearance was selective and cannot be attributed to volatility. Indeed, of the chlorinated solvents, only 1,1-dichloroethane was left whereas trichloroethylene and tetrachloroethane, which are less volatile than 1,1-dichloroethane, had essentially disappeared. The samples were obviously anaerobic as they had a very noticeable odour of volatile fatty acids. On the contrary, aromatic hydrocarbons which are easily biodegraded under aerobic conditions but not under anaerobic conditions, were persistent (Barker et al., 1987)

Table 1. Volatile Organic Compounds in Guelph and Muskoka Leachates

Sample Name	Guelph leachate	Guelph Leachate	Muskoka Leachate
Sampling Date	1988	1989	1989
Concentration	ug/L	ug/L	ug/L
CHLOROMETHANE	60	9	
VINYLCHLORIDE	14	23	
BROMOMETHANE			
CHLOROETHANE	26		
DIETHYLETHER	10	181	67
1,1-DICHLOROETHENE		34	
DICHLOROMETHANE	131	1008	57
T-1,2-DICHLOROETHENE		4	
1,1-DICHLOROETHANE	108	43	25
C-1,2-DICHLOROETHENE	29	205	10
THF			
CHLOROFORM			
1,1,1-TRICHLOROETHANE			
CARBON TETRACHORIDE			
BENZENE	23	19	18
1,2-DICHLOROETHANE	14	8	
TRICHLOROETHYLENE	67	51	
1,2-DICHLOROPROPANE			
DIBROMOETHANE		20	
T-1,3DICHLOROPROPANE			
TOLUENE	85	201	263
C-1,3DICHLOROPROPANE			
1,1,2-TRICHLOROETHANE			
TETRACHLOROETHENE	15		
DIBROMOCHLOROMETHANE			
DIBROMOMETHANE			
CHLOROBENZENE			
ETHYLBENZENE	83	80	35
M+P-XYLENE	158	148	66
O-XYLENE	96	85	37
STYRENE		14	
BROMOFORM			
CUMENE		2	2
1,1,2,2-TETRACHLOROETHANE			
PROPYLBENZENE		2	3
3+4-ETHYLTOLUENE	22	13	14
2-ETHYLTOLUENE	19	6	6
TRIMETHYLBENZENE	53	17	23
1,3-DICHLOROBENZENE			
1,4-DICHLOROBENZENE			
1,3-DIETHYLBENZENE			
1,2-DICHLOROBENZENE			
1,4-DIETHYLBENZENE			
1,2-DIETHYLBENZENE			

A blank indicates none detected

After four months, some of the lysimeters were showing the evidence of toluene breakthrough (Table 3). This has important implications for the impact of landfill leachate application to soils on groundwater contamination. If this breakthrough is observed after four months in lysimeters that contain a 30 cm clay layer, it is very likely that usual clay caps may not be sufficient to retain organic contaminants.

The season had been very dry and very little leachate was collected, therefore the study was repeated for a second season.

Table 2. Irrigants sampled on October 6, 1988, 4 months after the beginning of experiment.

LYSIMETER NUMBER CONCENTRATION	8 st ug/L	15 pl ug/L	19 pl ug/L	1 st ug/L
VINYL CHLORIDE		7	3	
DICHLOROMETHANE				3
1,1-DICHLOROETHANE	4	40	13	13
BENZENE	12	16	17	11
DIBROMOMETHANE	4			
TOLUENE	48	100	115	62
ETHYL BENZENE	17	43	44	22
m+p-XYLENE	55	85	99	65
o-XYLENE	25	43	45	31
TRIMETHYL BENZENE	3	3	4	3
DIETHYL ETHER	149	170	170	183

- a blank indicates none detected

Table 3. Effluents, October 1988.

LYSIMETER NUMBER CONCENTRATION	15 pl ug/L	19 pl ug/L
BENZENE	1	1
TOLUENE	16	4
m+p-XYLENE	1	1

2nd Year of the Study

In the second year, the study was expanded to include two different leachates. The leachates were analysed for volatile organic compounds and the results are listed in Table 1. The composition of the Guelph leachate was similar to that in the first year of study. The Muskoka leachate contained much fewer chlorinated organic compounds.

The results of the analyses of the lysimeter effluents are listed in Table 4. Breakthrough of the contaminants occurred much more rapidly than in 1988, partly because of the weather which was less conducive to evapotranspiration, and partly because irrigation was done to saturation. It is also interesting to note that almost all contaminants came through simultaneously and less soluble components such as dichloromethane were not significantly retarded compared to diethyl ether. This is most evident in sample 19 where effluent concentration were approching the irrigant concentrations. This would be the behaviour expected in the case of the formation of a fissure in the clay. Otherwise compounds would be expected to breaktrough sequentially, according to their retardation factors.

Table 4. Effluents 1989

LYSIMETER NUMBER	3 pl Guelph		5 st Muskoka		19 pl Guelph		9 st Muskoka
DATE	Jul 25	Aug 10	Jul 25	Aug 10	Jul 25	Aug 10	Aug 10
CONCENTRATION	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
VINYL CHLORIDE							
CHLOROMETHANE					3		
DIETHYLETHER	3				18	27	
1,2-DICHLORO-1,1,2-TRIFLUOROETHANE					3	71	
DICHLOROMETHANE	228	190			1072	726	
T-1,2-DICHLOROETHENE					2	4	
C-1,2-DICHLOROETHENE	2				25	35	
TOLUENE					6	80	2
ETHYL BENZENE							5
M+P-XYLENE			16		1	1	19
O-XYLENE			8		1	1	5

- a blank indicates none detected

Figure 1

Aromatic Compounds in Irrigant 3PL

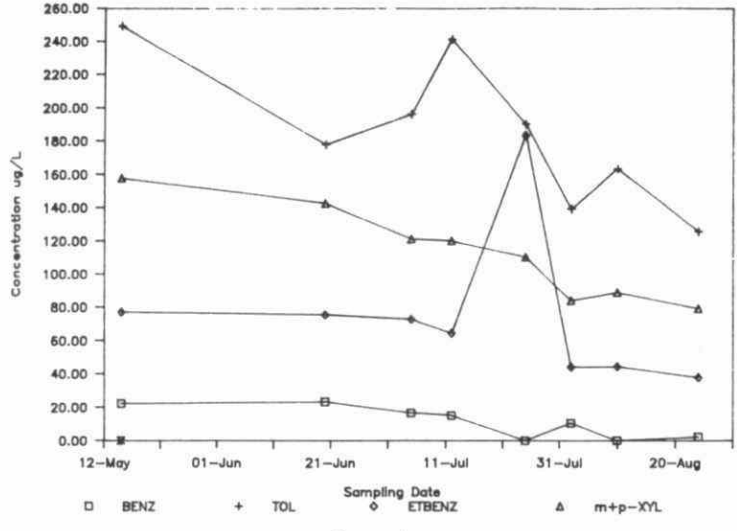
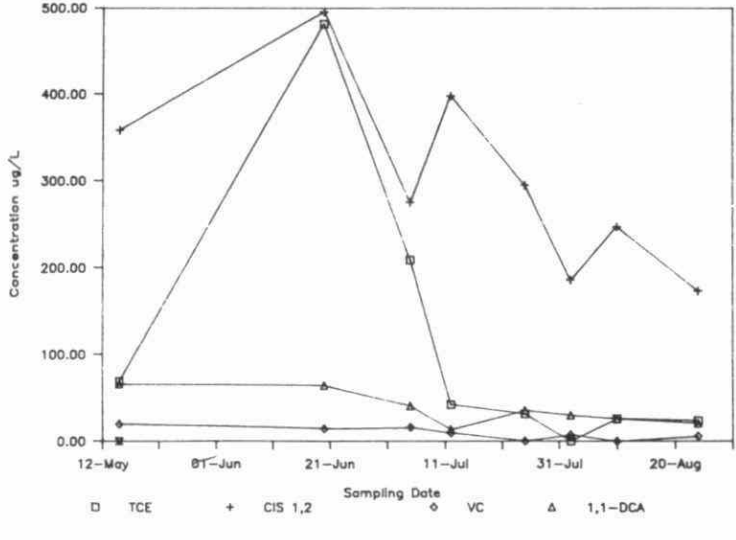


Figure 2

Chlorinated Compounds in Irrigant 3PL



As in the first year of study, the degradation of organic solvents in the irrigant holding tanks was selective. Volatile fatty acids were measured: acetic acid ranged from 2900 to 4300 mg/L, propionic from 1000 to 1500 mg/L and butyric from 250 to 500 mg/L. This induicates that anaerobic conditions were prevalent in the holding tanks. The degradation of aromatic compounds is depicted in figure 1, and that of chlorinated hydrocarbons in figure 2. The disappearance of chlorinated compounds with the exception of 1,2-dichloroethane was constant, while aromatic hydrocarbons remained relatively stable.

In addition, Freon-113 was spiked into the holding tanks and its concentration was followed over the same period. One of the problems was to reduce the variability between replicates. Since Freon-113 is only sparingly soluble in water and is denser than water, it was difficult to ensure complete dissolution and get a measure of its initial concentration.

Although disappearance of the substrate is often used as a measure of degradation, a better indicator of biological degradation is the appearance of metabolites. Lesage and Jackson (1989) proposed a pathway for the anaerobic degradation of F-113 which involves reductive dechlorination followed by elimination (Fig. 3). This pathway is similar to the transformation of trichloroethane to vinyl chloride (Vogel and McCarty, 1987).

After two weeks of incubation, both F-123a and F-1113 were found in the holding tanks. The product distribution in the different replicates is shown in Fig.4a, and the change with time in one lysimeter in Fig 4b. The same products were observed in contaminated groundwater from a landfill (Lesage et al., 1989). Experiments conducted using sulfate reducing and methanogenic bacteria in fixed biofilm reactors have also produced F-123a (Bouwer and Lew, 1989). This is another example of bioactivation, since, analogously to the production of vinyl chloride from perchloroethylene, the metabolite chlorotrifluoroethene is more toxic than its parent compound (LD_{50} in rats 268 mg/kg, Sax 1984).

Fig. 3 Metabolic pathways of Freon-113 (Lesage et al.1989)

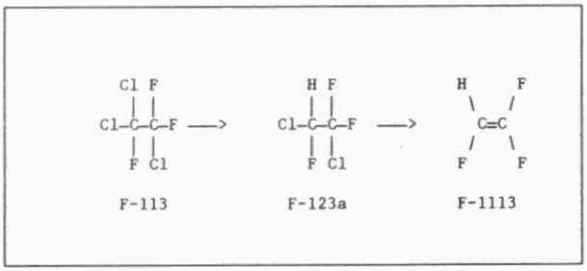
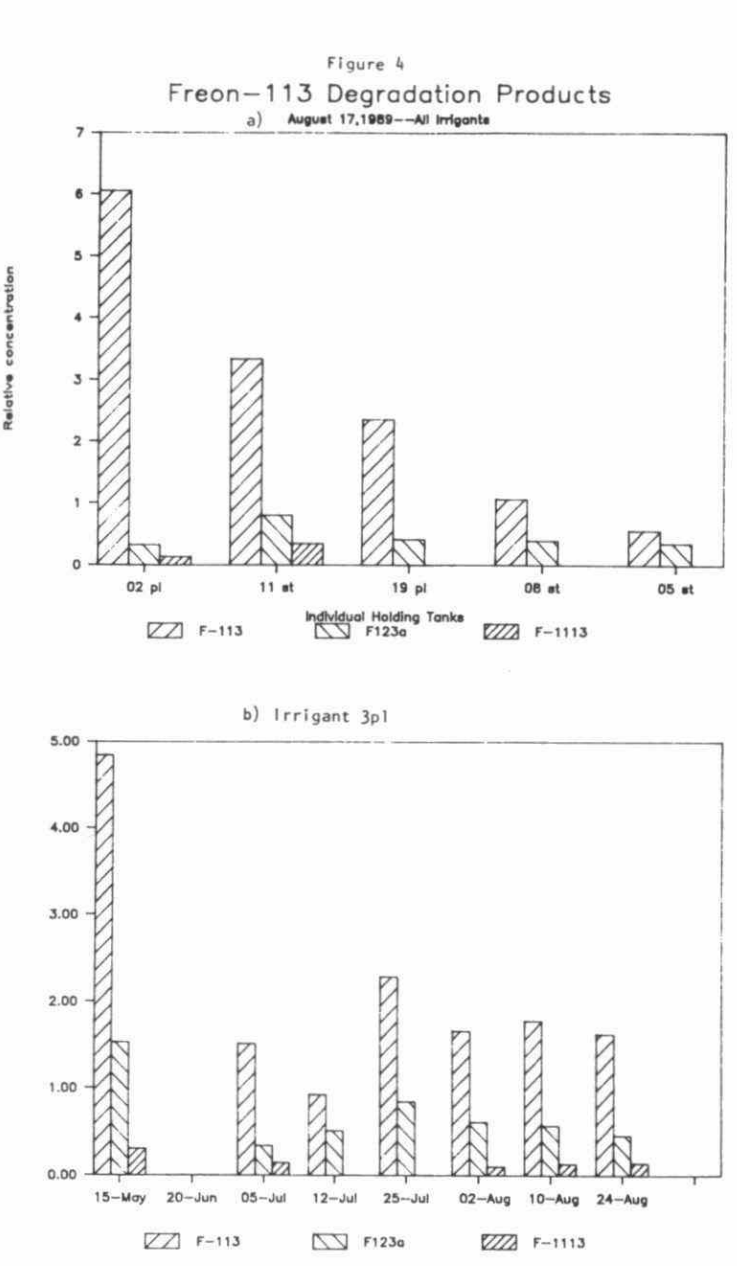


Figure 4


Freon-113 Degradation Products
a) August 17,1989--All Irrigants
Relative concentration
0
1
2
3
4
5
6
7
02 pl
11 st
19 pl
08 st
05 st
Individual Holding Tanks
F-113
F123a
F-1113
b) Irrigant 3pl
0.00
1.00
2.00
3.00
4.00
5.00
15-May
20-Jun
05-Jul
12-Jul
25-Jul
02-Aug
10-Aug
24-Aug
F-113
F123a
F-1113

CONCLUSIONS

These findings are of interest for the management of landfill leachates because an anaerobic incubation period allows for the degradation of most of the chlorinated solvents. This study also however shows that clay cannot be relied upon to contain dissolved organic wastes when applied on top of clay soil as irrigants.

ACKNOWLEDGEMENTS

The collaboration of Ms. Philippa Cureton of the University of Guelph is greatly appreciated. Thanks are also due to the laboratory services of Environment Canada's Wastewater Technology Center, for the analysis of volatile fatty acids.

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C10

PHYSIOLOGICAL AND SPECTRAL RESPONSES OF SUGAR MAPLE (Acer Saccharum Marsh.) TO MSW LEACHATE SPRAY IRRIGATION

S.C. Shrive, R.A. McBride and T.J. Gillespie
Department of Land Resource Science,
University of Guelph, Guelph, Ontario, N1G 2W1

ABSTRACT

Foliar gas exchange, water relations and spectral properties of understory sugar maple (Acer saccharum Marsh.) sapling leaves were studied in a natural forested ecosystem subjected to spray irrigation of municipal solid waste (MSW) landfill leachate and compared to similar measures taken from leaves of unirrigated saplings. Photosynthetic rates in irrigated saplings were reduced 34% to 53% in comparison to unirrigated sapling rates. Similarly, water use efficiency of sapling leaves subjected to direct leachate exposure dropped an average of 70%, while transpiration rates were similar to, and leaf temperatures were 20% higher than, those found in unirrigated leaves. Spectral patterns of understory leaves, distorted because of the accumulation of leachate precipitate residues on the adaxial surface, demonstrated increased absorbance in the near infrared waveband and reduced reflection in visible wavebands compared to abaxial surfaces. The adaxial spectral properties of mid-canopy leaves (above maximum spray height) of mature sugar maple trees were not distorted by these residues and revealed spectra that suggested increased nitrogen uptake and benefit derived from leachate irrigation. These findings on leaf tissue integrity and energy budgets are discussed in terms of the implications for design of leachate treatment and disposal systems on land and for forest ecology in general.

1. INTRODUCTION

Atmospheric precipitation percolating through municipal solid waste (MSW) landfills can enhance the decomposition, transformation and mobility of many chemical constituents in the refuse cell and lead to contamination of groundwater flow systems. Unless intercepted, these fugitive leachates can migrate further into the hydrologic cycle and have significant deliterious effects on surface aquatic ecosystems. Under certain site conditions, the quantities of leachate generated far exceed that which can be handled by engineered, on-site treatment facilities such as stabilization lagoons and anaerobic digestors. Consequently, alternative treatment and disposal options have been sought, particularly in remote areas. One method which has been investigated in Europe (Harrington & Maris 1986) and the U. S. (Menser et al. 1983) is slow rate infiltration (irrigation) of leachate in forested ecosystems or pre-prepared grass sward sites based on the principle of using the soil and vegetation as "living filters".

Land treatment of municipal sewage wastewaters in forested ecosystems has received considerable research effort (Anonymous 1985; Brockway 1988) and general land application methodologies for wastewater have been recently reviewed (Zirschky et al. 1986). The practice of MSW leachate treatment and disposal by irrigation on land, however, is relatively recent and the

effects on terrestrial ecosystems have not been adequately investigated. Slow rate infiltration land treatment, particularly by the spray irrigation method, is viewed as a potentially effective means of MSW leachate treatment and disposal because high levels of atmospheric evaporation can be attained thus maintaining the aerobic soil environment necessary for adequate renovation (McBride et al. 1989).

The composition of MSW leachate with respect to many of the essential plant nutrients varies greatly, with actual nutrient constituents dependent upon the initial composition of the landfilled refuse and the stage of decomposition (Barker 1987; Cyr et al. 1987). Heavy metals generally exist in trace amounts (Bennett et al. 1975). Studies have demonstrated that many of the chemical constituents of leachate can be taken up by plant roots and assimilated into vegetative tissue (Menser et al. 1983; Gordon et al. 1989a; 1989b). Micronutrients such as iron and manganese, however, can be present at toxic levels (Table 1) and rates of leachate application may, by necessity, be intolerably high for many indigenous plant species. Thus, evidence of vegetation stress has been observed with the shifting of plant stand composition towards hydrophyllic and pollutant-tolerant species. To fully assess the suitability of the land treatment and disposal option, information is required on the sources and mechanisms involved in vegetative stress development, the actual physiological effects and the threshold levels of vegetative tolerance to leachate application.

The importance and interpretation placed on a plant's positive or negative response to altered external conditions is greatly influenced by the response parameter measured. In an extensive review of woody species' responses to pollution, Kozlowski & Constantinidou (1986) suggest that relative growth rate and foliar injury are preferred measures of response to pollution exposure in trees. The determination of changes in physiological processes is of little relevance because of their extreme sensitivity to other environmental factors. Although effective in quantifying forest decline and identifying characteristic physical extremes of tree response, however, growth rates and some measures of physical injury require longer term measurement or exposure to inordinately high concentrations of pollutants. These measures are, therefore, quantifying overall resistance (including avoidance mechanisms) and not specifically tolerance. The latter implies a capacity to degrade and detoxify, an obvious objective of leachate application on vegetated land surfaces. Simultaneous measurements of physiological processes and foliar structure, as opposed to longer term measures of vegetation response (i. e. percentage of canopy affected), provide a response range and thus allow investigation of threshold levels and a meaningful indication of overall plant tolerance.

Reports on research confounded by the effects of uncontrolled and variable environmental factors, and the apparent inability to distinguish the effects of these environmental parameters from the stress-related responses of interest, may have been overemphasized, particularily for photosynthetic and transpirational response. For example, in a study of seasonal patterns of photosynthetic capacity in sugar maple (Acer saccharum Marsh.), oak (Quercus sp.) and American beech (Fagus grandifolia Ehrh.), Jurik (1986) found maximum CO_2 exchange rates and maximum stomatal conductance values to be constant from the time of full leaf expansion to senescence. This condition allows for the elimination of time as a variable,

Table 1. Chemical composition from a 1988 sampling of leachate from the Muskoka Lakes MSW landfill site, Ontario.

Chemical Constituent[1]		Volatile Organic Compound[3]	
NO_3	0	Benzene	4.2
NH_4	103	Chloroform	2.0
PO_4	0	Ethylbenzene	15.0
SO_4	0	Methylene chloride	100.0
Cl	98	Tetrachloroethylene	2.5
Mg	32	Toluene	560.0
K	114	Trichloroethylene	13.0
Na	41	Xylenes	36.0
Fe	37.5		
Mn	6.77		
Ni	1.46		
Cd	0.12		
Cu	0		
Pb	0		
Zn	2.67		
TOC[2]	2446		
pH	5.44		

[1] in units of $\mu g\ ml^{-1}$ with the exception of pH
[2] TOC: Total organic carbon
[3] in units of $\mu g\ l^{-1}$. Other volatiles may be present at levels below detection limits.

and meaningful measurements of tolerance and physiological response to stress can then be obtained over a succession of shorter term experiments when treatments are compared to controls under equivalent environmental conditions. Thus, measurement of gas and vapour exchange rates and the observation of the more symptomatic effects of physiological disturbance or benefit expressed through leaf optical properties (cf. Grant 1987) can provide a basis for tolerance studies. This approach enables an early characterization of forest decline or benefit before visible symptoms have appeared.

The present study was undertaken to determine the effects of spray irrigation of MSW leachate on foliar gas and vapour exchange and spectral properties in a mixed hardwood forest ecosystem and to interpret the findings in light of the altered soil and atmospheric environments created by such treatment.

2. MATERIALS AND METHODS

2.1 Site Description

The Muskoka Lakes sanitary landfill, located near Port Carling in the District Municipality of Muskoka, Ontario, is one of the few known locations in Canada where large-scale spray irrigation on land is used by the municipality as a treatment and disposal method for MSW leachate. At the time of the present study, the facility consisted of a network of 72 overhead spray irrigation nozzles drawing leachate from two 400,000 l stabilization lagoons where some unaided anaerobic digestion and gas-stripping pretreatment occurs. The spray area covered about 4.3 hectares of mature mixed hardwood forest, predominantly shade-tolerant American beech and sugar maple, with the latter species being prevalent in the understory. Daily spray application of leachate on to the forest floor and understory vegetation during the 7-month (April-October) spray season deposits a ferrihydrite-based residue on plant leaves to the point where the entire adaxial surface is irreversibly stained throughout the growing season.

In May, 1988, environmental control and spray treatment plots with similar subsurface stratigraphies, southeast aspects and Podzolic soil types (A.C.E.C.S.S. 1987) were established. The understory of both plots was largely composed of sugar maple saplings of 7 to 10 years of age which received maximum available insolation for at least 5 hours per day. The control area was suitably distanced from any influence of spray irrigation, past or present, while the saplings and soil surface in the treatment area received direct leachate application from two spray nozzles, each with non-overlapping discharge radii of about 16 m. The treated area has been subjected to seasonal (April-October) leachate application rates averaging approximately 14,000 l ha^{-1} d^{-1} since 1982 (Gordon et al. 1989a).

2.2 Foliar Gas Exchange Rate Measurement

In situ measurements of individual leaf gas and vapour exchange rates were made with a LI-COR model 6000 portable photosynthesis system and infrared CO_2 gas analyzer. The system calculates the stomatal conductance

for water vapour and the CO_2 exchange rate based on changes in the levels of these gases in a closed 1 litre polycarbonate cuvette over a 63 s period. Levels of incident photosynthetically active radiation (PAR) were measured by a LI-COR LI-190S quantum sensor. The system also contains a contact thermocouple for abaxial leaf temperature measurement and a relative humidity sensor. These measures are used in the calculation of stomatal conductance and transpiration rate. Carbon dioxide drawdowns were maintained in the recommended 20 - 30 ppm range and representative individual measurements demonstrated a linear relationship between CO_2 concentration and time. In this manner, the accuracy of photosynthetic rate measurements is maintained within 10% (Dwyer & Stewart 1986) and mean values of all measured parameters taken over each individual leaf measurement period were used in subsequent analyses. Some researchers (cf. Idso et al. 1988) have expressed concern over the accuracy of stomatal conductance values obtained in a closed cuvette system because the method alters the natural ambient environment. These concerns may be valid if the values obtained were to be extrapolated to estimate total canopy fluxes, but on a comparative basis, the accuracy of the method is adequate for determining relative treatment effects.

Measurements from mature leaves within five nodes of the apical meristem of understory saplings were taken on three cloud-free days (July 6, Aug. 16, Aug. 30) between 0800 and 1500 hours EST during the 1988 growing season. Three measurements from separate leaves of randomly selected saplings in each of the control and treatment plots were averaged to obtain values that were deemed representative of the parameter levels at a given level of PAR irradiance. Between individual measurements, the cuvette was kept shaded and the system was flushed to ambient CO_2 levels of 340 to 350 ppm.

2.3 Spectroradiometric Measurement of Foliage

A LI-COR model LI-1800 spectroradiometer fitted with an integrating sphere was utilized for determination of the leaf optical properties. These included hemispherical reflectance (compared to a barium sulphate standard), transmittance and absorbance (absorbance = 1 - reflectance - transmittance) of light in the visible and near infrared wavelengths (400 - 1100 nm) at 1 nm resolution.

For understory saplings in the treatment area, 8 equally spaced transects were set out along the radii of the same 2 spray nozzle trajectories used for the foliar gas exchange measurements. Intact leaves were collected for analysis from the third node below the apical meristem of saplings at 15 m and 2 m from the spray nozzle along these transects. These distances represented variable per unit area rates of leachate application and thus variable densities of the adaxial surficial deposit of leachate precipitate residue. In addition, 16 leaf samples from similar nodal positions were collected from randomly selected understory saplings in the control area. These samples were obtained on August 31, 1988.

In the spray treatment and control areas, intact overstory leaves at about 12 m above the forest floor were pruned from mature sugar maple trees. In the spray treatment area, the root systems and lower trunks of these trees are directly exposed to spray irrigation, but the leaves themselves

are situated above the maximum spray height and do not come into direct contact with the effluent spray. Nevertheless, mature tree leaves may be vulnerable to aerosol effects of the spray irrigation system, including exposure to many of the volatile organic constituents (e.g. BTX compounds). A total of 15 leaf samples were collected in each of the control and treatment plots on each of two dates, July 6 and August 16, 1988.

Individual leaf samples were sealed in plastic bags and immediately cooled to 5°C. This storage environment was maintained until measurement in the integrating sphere was performed in an atmospherically controlled laboratory setting within 24 hours of pruning. Such handling of leaf tissue does not appear to significantly alter its spectral properties (Daughtry & Biehl 1985) and ensures more accurate equipment performance than would be possible by conducting these measures in the field.

Total annual precipitation for the area in 1988 as recorded by the Muskoka Airport meteorological station in nearby Bracebridge was 1147 mm, heavier than the 30 - year normal precipitation of 1009 mm. Monthly levels of 46.5 mm (March), 92.4 mm (April), 62.6 mm (May), 65.0 mm (June), 121.4 mm (July) and 97.0 mm (August), however, were 70%, 126%, 79%, 79%, 157% and 109%, respectively, of the 30-year monthly precipitation normals. The first half of the growing season in 1988 was thus characterized by a short-fall in precipitation which, when combined with abnormally high atmospheric vapour pressure deficits, created a significant soil moisture deficiency.

3. RESULTS AND DISCUSSION

3.1 Foliar Gas Exchange and Water Relations

The effects of early season atmospheric and soil moisture deficiencies and a gradual reduction in this moisture stress later in the season are evident in Fig. 1. High average vapour pressure deficits (VPD) on July 6 restricted mean stomatal conductance values (g) in treated and control saplings to 0.150 and 0.258 cm s^{-1}, respectively. The stomatal response to a decrease in the water stress on subsequent measurement days is apparent, with g-values for irrigated trees reaching maximum means of 0.423 cm s^{-1} on Aug. 16, and 0.602 cm s^{-1} for control trees on Aug. 30. The control stomatal conductance mean for July 6 was 58% lower and the atmospheric VPD was more than 100% greater than the corresponding Aug. 30 data. Bahari et al. (1985) reported a 48% decrease in daily mean values of g in moisture-stressed sugar maple saplings compared to well-watered controls over similar VPD ranges, but at higher absolute levels of VPD. Through boundary line analysis of sugar maple leaf water relationship parameters, Hinckley et al. (1978) determined the effective threshold level of VPD on g to be about 2.0 kPa over soil water potentials ranging from -40 kPa to -510 kPa. This threshold level is corroborated in the present study when early season maximum measures of g in control saplings under a higher water stress are compared to minimum measures made later in the season when the VPD fell to below 2.0 kPa.

In a study of the effects of insecticide sprays on pecan tree (Carya illionoensis [Wang.] K. Koch) leaves, Wood & Payne (1986) found reduced rates of net photosynthesis (P_N) in sprayed leaves while differences in g

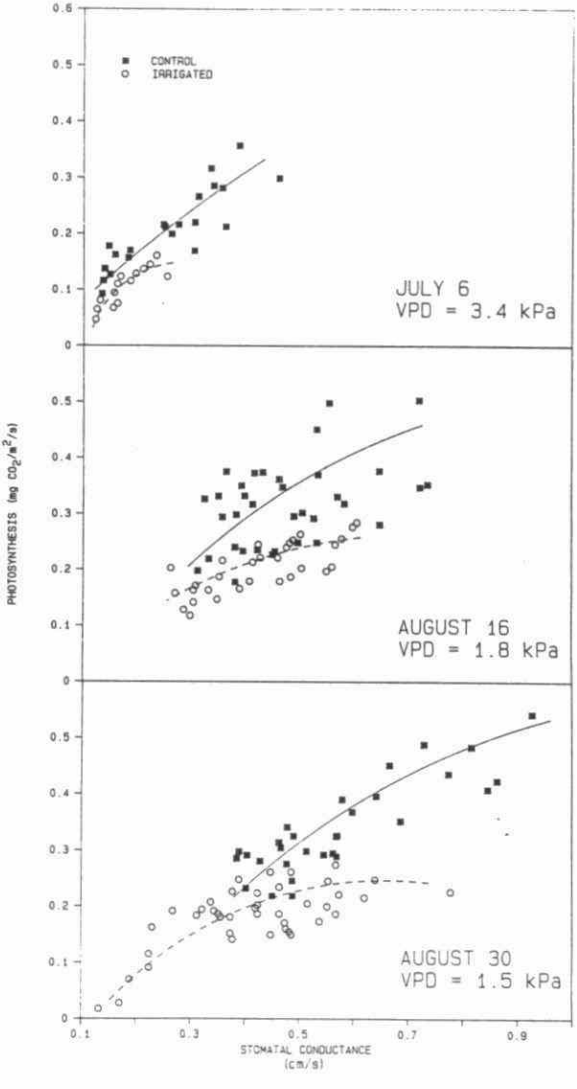

Fig. 1. Photosynthesis as a function of stomatal conductance for leaves of irrigated and unirrigated sugar maple on 3 dates in 1988. VPD = average vapour pressure deficit.

were not statistically significant from those found in unsprayed leaves. A similar trend occurred at the Muskoka Lakes site where noticeably lower rates of P_N are also apparent in spray-irrigated saplings compared to those of control saplings at similar g levels (Fig. 1). Data from the simple regressions of P_N on g (log transformed) for the three dates (Table 2) additionally demonstrate the generally lower rates at which P_N rises with increasing stomatal aperature in irrigated saplings (i.e. the b_1 parameters). Similarities in the values of intercept and slope within each of the treatments over the study period indicate two distinct and consistent overall photosynthetic trends with absolute levels of both regression parameters being lower in the irrigated saplings. Barlow (1983) demonstrated that the P_N response to g in slowly-stressed (i.e. acclimatized) plants is linear and is evidence of a co-ordinated response by the leaf in controlling the levels of these parameters. Leaves of plants subjected to a more severe and immediate stress have a greater non-linear response and the P_N/g ratio (i.e. slope) does not remain constant, as with the irrigated saplings in Fig. 1.

Water use efficiency (WUE), the ratio of CO_2 assimilated to water lost through transpiration, was lower in irrigated saplings over the sampling period (Table 3). The later measure of irrigated WUE, however, exceeds that of the earlier season control measure made under an abnormally high VPD. Unless transpiration (E) is lowered proportionally in response to decreases in stomatal conductance and/or the leaf temperature, reduced WUE may be expected in irrigated saplings because of the lower overall P_N found in the treatment. Transpiration data (Table 3) indicate that mean control E values did not differ significantly ($P<0.01$) within treatments, while irrigated sapling E rose and then returned to former levels ($P<0.01$) over the sampling period. Transpiration rates differed between control and irrigated saplings one third of the time, with E in irrigated saplings being higher only on Aug. 16. In addition, measures of irrigated sapling E generally had a wider range and variability than those of control saplings.

3.2 Leaf Spectral Properties

3.2.1 Understory

The quality and quantity of spectral reflectance, transmittance and absorbance of light by leaves in the visible and near-infrared (400-1100 nm) wavelengths provide a basis for characterizing foliar structure and symptomatic interpretation of plant health (Gates et al. 1965; Knipling 1970; Horler et al. 1983). The adaxial spectral reflectance of control understory sugar maple leaves (Fig. 2) provides a typical pattern, with increased reflectance in the green band centred at about 550 nm (nitrogen content, non-absorbance of chlorophyll), a reflectance minimum at about 680 nm (chlorophyll absorption maximum), a rapid rise in reflectance around 700 nm (the "red edge") and a reflectance shoulder at 750-1100 nm (cell structure and integrity, water content). At positions closer to the spray nozzles in the treatment plot, the amount of leachate intercepted by the leaves increased as did the density of the ferrihydrite-based residue precipitated on the adaxial leaf surface. This progressively altered the spectral reflectance and distorted the characteristic spectra. Gausman (1982) found similar spectral distortions in green, bronze and common red cotton (Gossypium hirsutum L.)leaves and Boyer et al. (1988) observed the

Table 2. Results from simple regression of photosynthetic rate (mg CO_2 m^{-2} s^{-1}) of sugar maple against the logarithm of stomatal conductance (cm s^{-1}) for three dates in 1988.

		Least Squares Parameter Coefficients[1]	
Date	Treatment	b_0 (intercept)	b_1 (slope)
July 6	Control	0.429a	0.154a
	Irrigated	0.254b	0.081b
August 16	Control	0.432a	0.153a
	Irrigated	0.303b	0.112b
August 30	Control	0.451a	0.205a
	Irrigated	0.316b	0.144b

[1]all regressions were significant at $P < 0.001$
Within dates, parameter estimates between treatments followed by different letters are significantly different at $P < 0.01$

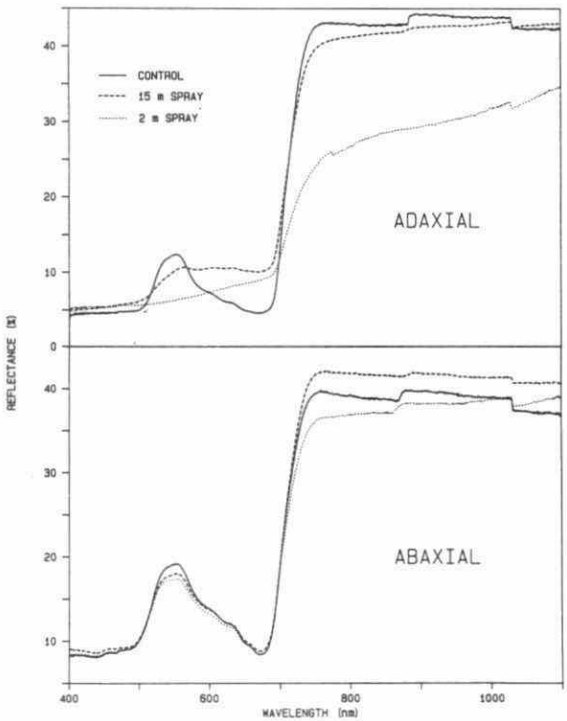

Fig. 2. Spectral reflectance patterns for adaxial surfaces (top) and abaxial surfaces (bottom) of leachate irrigated (variable intensity) and unirrigated understory leaves of sugar maple at Muskoka Lakes on August 31, 1988.

trend during pin oak (Quercus palustris Muenchh.) leaf senescence, but these altered spectra were attributed to masking by secondary pigments such as cartenoids and anthocyanins and a seasonal breakdown of chlorophyll. Of note here, however, is the reduced reflectance of the sprayed leaves in the near-infrared waveband, suggesting a possible upsetting of the normal leaf energy balance and leading to higher leaf temperatures. The spectrum also demonstrated a greater reflectance at the chlorophyll well, indicating a reduction in the photochemical energy required for photosynthesis. In this waveband, the 15 m treatment reflectance was higher than that of the 2 m treatment, possibly because of the less dense surface precipitate on leaves at the circumference of the spray trajectory.

The abaxial surfaces of sprayed leaves are not as vulnerable to direct leachate exposure or precipitate residue formation and displayed a more characteristic reflectance response (Fig. 2). Abaxial reflectance in the visible range was greater than that of adaxial reflectance in control leaves while the the converse was true for reflectance in the near-infrared. The latter response is a function of differences in the refractive properties of the closely packed palisade tissue of the upper surface and the smaller, loosely packed cells of the lower (Woolley 1971; Gausman 1984). The greater reflectance of leaf abaxial surfaces in the visible range is attributable to epidermal configuration in relation to adjacent cells (Woolley 1971), with the abaxial epidermis backing on more air space than the adaxial outer cell layer, thus increasing its refractive and reflective properties. Significant decreases were found in the abaxial reflectance of sprayed leaves at the 550 nm wavelength (Table 4), suggesting an alteration or breakdown of cellular structure in this area. Reflectance at 680 nm was significantly different only for the 15 m spray treatment, this being 5% higher than that of control and 2 m sprayed leaves. Reflectances at the 750 nm wavelength were dissimilar, however, with response rising and then falling significantly across increasing treatment levels. This suggests an initial closer packing of abaxial cells in leaves of the 15 m treatment and a subsequent deterioration with the increased foliar contact and leachate residue accumulation present on adaxial surfaces found at the 2 m distance.

3.2.2 **Overstory**

Reflectance patterns of mid-canopy leaves from mature sugar maple trees in control and spray irrigated plots showed none of the spectral distortion associated with the leachate precipitate present on understory adaxial surfaces. A nearly identical response was demonstrated by leaves of control and irrigated trees on July 6 and reflectance factors for characteristic wavelengths (Table 5) indicated a significant difference only in the chlorophyll well area (680 nm), where reflectance was very slightly greater in leaves from irrigated trees. By Aug. 16, this discrepancy had disappeared, with control reflectance levels higher than in those of irrigated tree leaves. Over this time, however, reflectance at the 550 nm wavelength was reduced and became significantly lower in leaves from irrigated trees. Decreases in adaxial reflectance in the 500-700 nm waveband have been indirectly correlated with increasing nitrogen content in leaves of corn Zea mays L. (Walburg et al. 1982), rice Oryza sativa L. (Shibayama & Akiyama 1986) and winter wheat Triticum aestivum L. (Hinzman et al. 1986). Through the study of reflectance properties and chemical constituents of dried hardwood leaf tissue, Card et al. (1988) found high correlations

Table 3. Water use efficiencies (mg CO_2 g^{-1} H_2O) and transpiration rates (mg H_2O m^{-2} s^{-1}) of irrigation and unirrigated sugar maple sapling leaves for three dates in 1988.

Date	Treatment	WUE	E		
			Mean	Minimum	Maximum
July 6	Control	3.21a (0.05)	51.10a (4.02)	24.87	83.50
	Irrigated	0.94b (0.37)	45.16a (4.73)	23.97	91.08
August 16	Control	6.64a (1.32)	50.78b (1.25)	37.31	69.77
	Irrigated	0.87b (0.42)	57.21a (2.82)	35.67	97.87
August 30	Control	13.14a (1.50)	46.92a (0.92)	35.62	60.85
	Irrigated	4.87b (0.68)	47.97a (1.46)	24.83	64.71

Parameter values within dates followed by different letters are significantly different at $P < 0.05$.

Table 4. Pooled means (standard errors) of reflectance factors (%) at three wavelengths for leaf abaxial surfaces of understory sugar maple under variable intensities of leachate deposit.

	Wavelength (nm)		
Treatment	550	680	750
Control	19.15a (0.28)	8.79b (0.15)	39.33b (0.29)
2 m spray	17.35b (0.21)	8.87b (0.12)	36.02c (0.53)
15 m spray	17.95b (0.27)	9.23a (0.12)	41.63a (0.28)

Means within wavelengths followed by different letters are significantly different at $P < 0.05$

between reflective response and predicted nitrogen content at 580 nm (r^2 = 0.90) and chlorophyll content at 680 nm (r^2 = 0.88). Although chemical analysis was not performed on leaves used for determination of reflective properties in the present investigation, previous studies at the Muskoka Lakes site (Gordon et al. 1989a) showed significant increases of up to 25% in the foliar nitrogen content of leachate irrigated sugar maple trees when compared to unirrigated controls. The dramatic decrease in reflectance in this waveband for leaves of irrigated trees in August (Table 5) supports this finding and demonstrates the temporal influence of leachate application over the spray application period. Also of note is the time required for the expression to develop, with the decreased reflectance (i.e. increased absorbance) at the 680 nm wavelength for irrigated trees over the season suggesting that nitrogen uptake by these trees is increasingly allotted to chlorophyll production.

The area of reflectance increase between 680 and 750 nm (the "red edge") has a parameter, λ_{re}, defined by Horler et al. (1983) as the wavelength of maximum slope. Its position is shown to be dependent on chlorophyll concentration, with increased width of the absorbance well causing a shift of the red edge and wavelength of maximum slope towards the red band. The results of first derivative reflectance spectra for the red edge component of mature tree leaves from the present study are shown in Fig. 3 and numeric values are given in Table 6. The significant red shift and decrease in maximum slope for irrigated trees in August tend to support the postulate of increased chlorophyll production in these trees.

A blue shift (i.e. toward shorter wavelengths) in the red edge of vegetative reflectance has been used in remote sensing applications to identify areas undergoing forest decline (Rock et al. 1988) or vegetation growing in soils overlying metal ore deposits (Collins et al. 1983; Singhroy et al. 1986). Although forest decline is visibly evident through increased crown dieback in irrigated areas at the Muskoka Lakes site and high concentrations of iron and other metals are present in the leachate being applied (Table 1), no evidence of a blue shift was observed in spectra of irrigated tree leaves during the 1988 field season. This may be because there was a significant moisture deficit initially in the growing period, and McBride et al. (1989) observed that over-irrigation of leachates during abnormally wet seasons is likely to be the most dominant factor contributing to the forest dieback observed at this landfill site. Foliage from leachate irrigated trees at this site and from associated greenhouse experiments has also demonstrated increased levels of iron (Gordon et al. 1989a; 1989b; Ont. Min. Env. 1988). If increased iron concentrations in plant biomass is causing stress, it was insufficient to influence the red edge parameters in the current study. In addition to a blue shift in the red edge, Schwaller et al. (1983) found significant increases in leaf relectance at 775 and 1000 nm in sugar maple saplings subjected to stress from heavy metal uptake. Visual inspection of these wavelengths for trees irrigated in August indicated a similar trend, but differences in reflectance at 770 nm were not statistically significant (Table 5).

3.3 Leaf Physiology and Spectral Response

Adaxial and abaxial absorbance spectra for leaves of understory sugar maple (Fig. 4) demonstrated an increasing absorbance of near-infrared

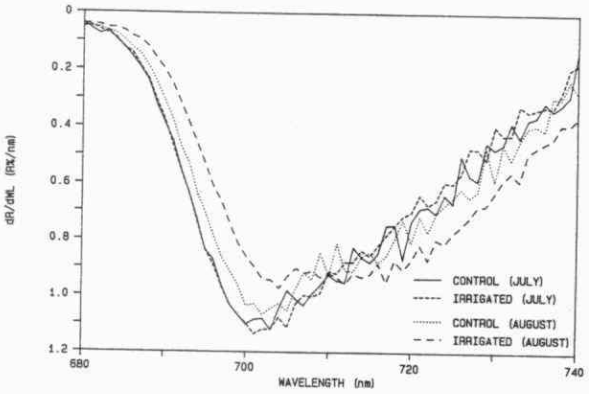

Fig. 3. First derivative spectra for the red edge component of reflectance for mid-canopy leaves of irrigated and unirrigated sugar maple trees on 2 dates in 1988.

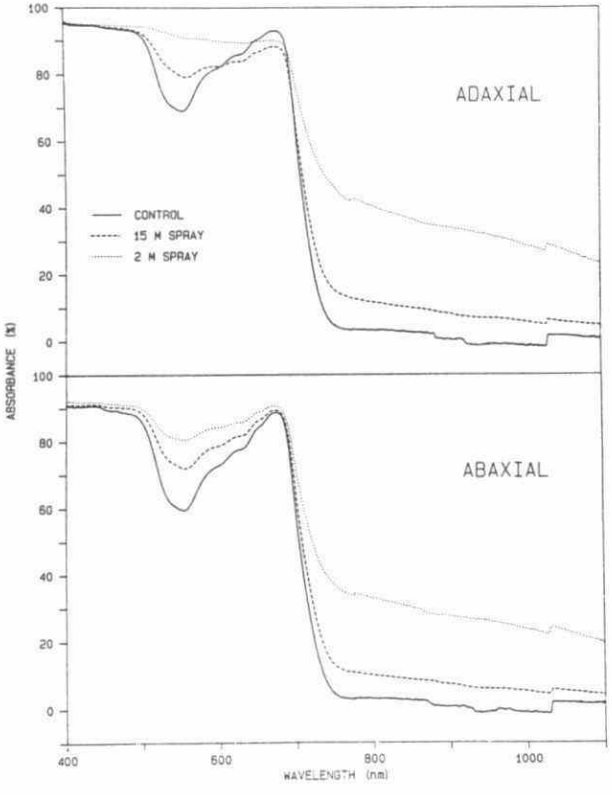

Fig. 4. Adaxial (top) and abaxial (bottom) absorbance spectra for leaves of leachate irrigated (variable intensity) and unirrigated understory sugar maple at Muskoka Lakes on August 31, 1988.

Table 5. Pooled means (standard errors) of reflectance factors (%) at three wavelengths for adaxial surfaces of mid-canopy leaves from irrigated and unirrigated sugar maple trees on two dates in 1988.

	Wavelength (nm)					
Date	550		680		770	
	Control	Irrigated	Control	Irrigated	Control	Irrigated
July 6	13.40a (0.37)	13.43a (0.34)	4.52bc (0.08)	4.85a (0.06)	44.49 (0.48)	44.30 (0.44)
August 16	12.52a (0.46)	10.39b (0.28)	4.75ab (0.07)	4.65b (0.06)	44.13 (0.31)	44.89 (0.39)

Treatment means within wavelengths and between dates followed by different letters are significantly different at $P < 0.05$

Table 6. Pooled means of red edge parameters and maximum slopes for adaxial surfaces of mid-canopy leaves from irrigated and unirrigated sugar maple trees on two dates in 1988.

Date	Treatment	λ_{re} (nm)	Maximum dR/dWL (R%/nm)
July 6	Control	703b	1.119a
	Irrigated	701b	1.134a
August 16	Control	702b	1.066a
	Irrigated	712a	0.956b

Parameter values followed by different letters are significantly different at $P < 0.05$

radiation with increasing adaxial deposition of leachate precipitate residue, thus possibly causing higher leaf temperatures. Measurements of leaf abaxial temperatures made over the study period (Table 7) indicated substantially higher surface temperatures in leaves of irrigated saplings compared to those of control saplings. While mean transpiration rates between the two treatments did not differ, maximums were higher in spray-irrigated saplings (Table 3). Berry & Bjorkman (1980) reported that stomata of well-watered plants in many species tend to remain open as temperatures increase beyond photosynthetic optima. In a study comparing dessication resistance mechanisms in hardwood species saplings, Wuenscher & Kozlowski (1971) showed that the dominant response in sugar maple to higher leaf temperatures is to increase transpiration rates rather than lower stomatal conductance. In the present study, however, factors contributing to the decrease in photosynthesis in irrigated saplings may include a reduction in stomatal conductance in association with a failure of transpiration rates to maintain leaf temperatures within the photosynthetic optimum.

The relationship between the temperature of the leaf and that of the air is considered as a function of PAR irradiance for the Aug. 30 data in Fig. 5. It can be seen that the escalation of this temperature differential is more rapid and linear in irrigated saplings than in control saplings where the rise is more suppressed and curvilinear, indicating a greater control over the temperature differential by leaves without leachate precipitate residues. In a review of plant water relationships and canopy temperatures, Jackson (1982) notes that differences between canopy and air temperatures (the stress degree day, or SDD) increase with increasing plant water stress and a reduction of available water in the soil for transpiration. In the present study, spray irrigated leaves demonstrated higher mean temperatures, but both control and treated leaves are seen to operate under similar ranges of leaf-air temperature differences. Table 6 demonstrates that air temperatures in areas of leachate spray irrigation are significantly higher than areas not receiving the treatment. This is surprising in view of the differences in moisture supplied, but may be a result of a general accumulation of residue on the forest floor in irrigated areas, leading to decreased albedo (i.e. increased absorbance of shortwave radiation) of the forest floor and thus a greater conversion of this energy to longwave radiation and heat. Increased infrared absorption and reradiation by the precipitate-prone understory leaves themselves may also contribute to this phenomenon. In turn, warmer temperatures may cause an increased VPD, imposing additional stress on saplings subjected to spray irrigation of leachate.

Photosynthetic rates in control saplings remained higher than those of irrigated saplings at corresponding differences in leaf-air temperatures on Aug. 30 (Fig. 6). The lower values of irrigated sapling P_N under higher air temperatures but similar leaf-air temperature differences may further support the postulate of reduced stomatal conductance in irrigated plots.

4. CONCLUSIONS

An investigation of the effects of MSW leachate application on forested ecosystem vegetation through simultaneous measurement of physiological

Table 7. Means (standard errors) of abaxial leaf temperatures and treatment plot air temperature in irrigated and unirrigated understory sugar maple on three dates in 1988.

Date	Treatment	Temperature (°C)	
		Leaf	Air
July 6	Control	32.36b (0.57)	31.89b (0.49)
	Irrigated	36.36a (0.77)	34.98a (0.55)
August 16	Control	24.55b (0.35)	23.39b (0.30)
	Irrigated	30.19a (0.54)	29.02a (0.45)
August 30	Control	21.79b (0.32)	21.07b (0.25)
	Irrigated	27.75a (0.34)	26.92a (0.30)

Parameter means within dates followed by different letters are significantly different at $P < 0.05$

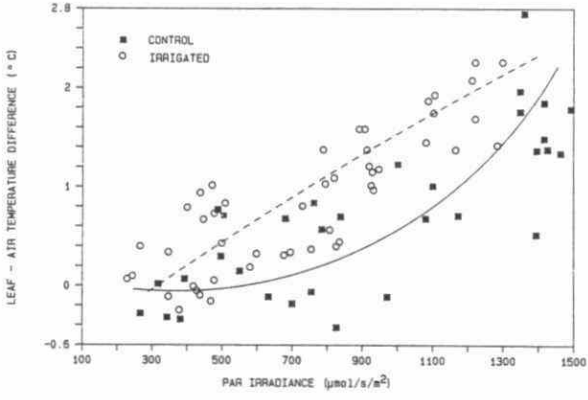

Fig. 5. Leaf-air temperature difference as a function of PAR irradiance in irrigated and unirrigated understory sugar maple sapling leaves at Muskoka Lakes on August 30, 1988.

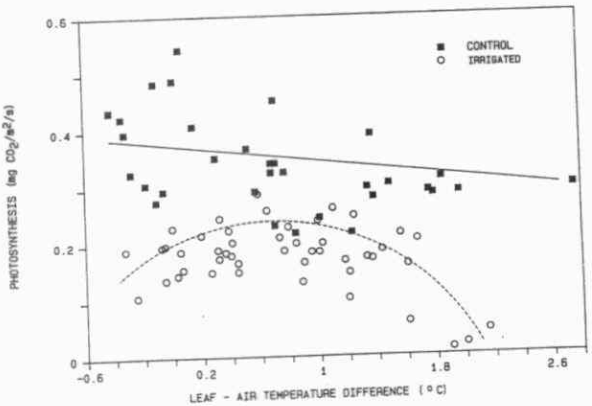

Fig. 6. Photosynthetic rate in relation to leaf-air temperature difference in irrigated and unirrigated understory sugar maple sapling leaves at Muskoka Lakes on August 30, 1988.

parameters over short-term intervals provides a characterization of plant response and permits an interpretation of factors relating to stress and/or benefit. This allows for a further assessment of wastewater management practices that would enhance leachate treatment and provide benefit to the recipient terrestrial ecosystem while identifying mitigating procedures to reduce deleterious effects.

The spectral response of mid-canopy leaves indicates that many of the mature trees subjected to spray irrigation at the Muskoka Lakes landfill site remain vigorous and may benefit from the added nitrogen levels and enhanced soil water availability as a result of leachate application. These measurements, however, were made in a season when abnormally low levels of rainfall occurred. If leachate application rates are not regulated in accordance with evapotranspiration demand and precipitation regimes, chronic excess soil water and poor soil aeration conditions will persist, inevitably leading to tree root anaerobiosis and the observed mature tree die-back (McBride et al. 1989).

Understory vegetation, on the other hand, is enduring considerable stress as a result of leachate application, due at least in part to the distortive qualities of the precipitate residue that develops on adaxial leaf surfaces. This residue alters the spectral quality and absorbance of incident radiation on leaves and their surrounding environment, causing significant deviations in energy balances and microclimate. This in turn leads to reduced sapling photosynthesis and ultimately, reduced growth and decreased likelihood of forest regeneration by understory release.

If application of landfill leachate to forest ecosystems is to be a considered seriously as a treatment and disposal option, then long-term management plans for terrestrial ecosystem use must be created before treatment commences and a full analysis of leachate characteristics and constituents should be performed in respect to pre-application treatment requirements and application method. If ecosystem integrity is to be maintained and leachate properties indicate a precipitate will develop as a result of spray application, then pretreatment or deployment of an alternative application methodology (i.e. trickle or sub-surface irrigation) might be necessary. Further study of these alternatives, their efficacy in the treatment of landfill leachate and their effects on recipient terrestrial ecosystems is required to fully realize the potential of this wastewater treatment and disposal option.

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C11

TRACE HEAVY METAL SPECIATION IN FOUR LANDFILL LEACHATES AND THE RETENTION OF LEACHATE CADMIUM BY SOIL

K. Bolton and L. J. Evans.

Department of Land Resource Science, University of Guelph, Guelph, Ontario

ABSTRACT

The composition and speciation of four southern Ontario municipal solid waste landfill leachates were investigated. Leachate samples were analyzed for major cations and anions together with trace heavy metals. Although the chemical composition of the landfill leachates was extremely variable, some general conclusions can be made. The leachates contained high concentrations of alkali and alkaline earth metals and of chloride ions. Some contained heavy metal concentrations that exceeded maximum acceptable levels for potable water. The equilibrium chemical computer model GEOCHEM was used to calculate the speciation of the landfill leachates. Alkali and alkaline earth metals existed primarily as uncomplexed metals while iron existed primarily as hydrolyzed species. Heavy metals existed as free metals or as complexes with carbonates, hydroxide, chloride or sulphate. Chloride complexes dominated the aqueous chemistry of leachate cadmium. The retention of cadmium has been investigated by adsorption experiments and initial results indicate that Cd adsorption increases with increasing pH.

INTRODUCTION

The disposal of solid waste in sanitary landfill sites has been used and will continue to be used extensively throughout Ontario. The major problem resulting from this method of waste management is the generation of large quantities of liquid leachate which subsequently move out of the fill and into the surrounding soil. It has been proposed (Harrington and Maris, 1986) that, since this leachate contains all of the essential plant nutrients, it would be practical to apply the liquid leachate to forested and agricultural ecosystems using slow rate infiltration land treatment. However, because the liquid leachate often contains high concentrations of organic and inorganic pollutants, our desire to solve one problem may, in fact, be creating another.

Chian and Dewalle (1976) have shown that the composition of landfill leachate from different sources is extremely variable. The variability in leachate composition is due to factors such as: size and composition of solid wastes, landfill age and degree of compaction and rainwater infiltration. Therefore before landfill leachates can be considered as a source of recycled plant nutrients it is important to investigate their composition and to calculate their metal speciation. This paper reports the results of a characterization of four southern Ontario landfill leachates. To simulate the chemical speciation of the landfill leachates the equilibrium chemical model GEOCHEM and the thermodynamic database GEODATA (Sposito and Mattigod, 1979) were used. Computer models like GEOCHEM allow the user to calculate the equilibrium speciation of the chemical elements in a soil solution.

Due to the presence of chemically reactive components, including clay minerals, humic materials and the oxides, hydroxides and oxyhydroxides of iron and aluminum, soil has the capacity to immobilize trace heavy metals. Chian and DeWalle (1976) reported cadmium concentrations in sanitary landfills in the range of 0.03 to 17 mg/l. Because of its environmental significance the interaction and retention of leachate Cd by the soil is also being investigated. This paper also presents the preliminary results of this investigation.

TRACE HEAVY METAL SPECIATION

Materials and Methods

Leachate samples were taken from four municipal solid waste landfill sites in southern Ontario. The four landfill sites sampled were the Essex County Sanitary Landfill No. 2(Leamington), the Hamilton-Wentworth Regional Landfill (Glanbrook), the Muskoka Lakes Landfill, and the City of Guelph Landfill. One litre samples were taken in the summers of 1988 and 1989. The samples were refrigerated and filtered through a 0.45μm millipore filter prior to analysis.

Atomic absorption spectroscopy was used to determine the concentrations of K, Na, Mg, and Ca. Concentrations of Ni, Cd, Fe, Mn, and Zn were measured using Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES). Phosphate and SO_4^{2-} were determined using Ion Chromatography while Cl^-, NO_3^- and NH_4^+ were determined by colorimetric methods. Total organic carbon, electrical conductivity and pH were also measured. In addition, a red precipitate found in the Muskoka leachate was characterized by scanning and transmission electron microscopy (SEM and TEM), energy dispersive spectroscopy and x-ray diffraction employing CuK∝ radiation.

The computer program GEOCHEM was used to calculate the chemical equilibrium composition of all the leachate solutions.

RESULTS AND DISCUSSION

Table 1 summarizes the chemical composition of the four leachate samples. Although the chemical composition of the leachates is extremely variable some general conclusions can be made. The leachates contained high concentrations of the major cations Mg, Ca, K, and Na. The leachate samples from the Guelph, Leamington and Glanbrook sites had high Cl^- concentrations. From an environmental point of view the heavy metal concentrations, particularly that of Cd, are of greatest concern. In all four leachates Cd concentrations exceeded the Ministry of the Environment's maximum acceptable potable water level of 0.005μg/ml (Ontario Ministry of the Environment, 1983).

Large quantities of a rust coloured solid were found in the Muskoka leachate and, due to the high iron concentration in this leachate (Table 1), the presence of an iron oxide was presumed. The x-ray diffractogram of the sample displayed a broad peak between 30 and 43°2θ . Scanning electron micrographs (Figure 1) revealed that the solid had a fine granular structure and energy dispersive analysis indicated a dominance of iron in the solid. These are characteristic of the poorly crystalline iron oxyhydroxide ferrihydrite.

Tables 2 and 3 show the predicted percentages of free and bound metals in the Muskoka and Guelph leachates, respectively, as calculated by GEOCHEM. The alkali and alkaline earth metals are predicted to exist primarily as uncomplexed metals while Fe exists entirely as a complex with carbonate or hydroxide. The heavy metals, apart from Cd, are precicted to exist primarily as free metals with a minor amount of anion complexation. Chloride concentration has a great impact on the amount of free Cd^{2+} present in the solution. The Guelph leachate has a very high Cl^- concentration and hence only 12 percent of the Cd is predicted to exist as a free metal while the relatively low Cl^- concentration in the Muskoka leachate results in almost 80 percent free Cd^{2+}. The distribution of Cd species at different pH values for the Guelph leachate is presented in figure 2.

LEACHATE CADMIUM

Materials and Methods

Soil samples were taken from the same four landfill sites sampled for leachate chemistry. At the Hamilton-Wentworth Regional Landfill two samples were taken, one from an undisturbed forested area (Glanbrook Ah) and the second from an adjacent grassed area (Glanbrook Ap). A sixth sample was taken from a site in the Regional Municipality of Niagara (Welland). Samples were taken from the A horizon of each profile. The samples were air dried, ground to pass a 2 mm sieve and passed through a sample splitter prior to storage. For the adsorption experiments subsamples were ground further using a hand held mortar and pestle.

Adsorption experiments were carried out in duplicate in 50 ml acid washed centrifuge tubes. Fifty to 200 mg of soil was added to the tubes along with 25 ml 0.01 M $LiClO_4$ solution. Appropriate quantities of 1 M LiOH or 1 M $HClO_4$ were added to this solution and equilibrated at 25°C for eight days to obtain nine pH levels in the range 3.5 to 8.0. After eight days of equilibration aliquots of a $CdClO_4$ solution were added to obtain Cd concentrations ranging from 0.06 to 0.2 mmol Cd/l. The solutions were equilibrated at 25°C for another 24 hours and then centrifuged at 8000 x g for 20 minutes. A 10 ml sample was filtered (0.45µm) for quantification of residual solution Cd by ICP-AES and a HACH free-diffusion junction electrode was used to measure pH on the remaining solution.

RESULTS AND DISCUSSION

Figures 3 and 4 show the pH-dependent adsorption behaviour of Cd for the Glanbrook Ap and the Guelph Ap horizons, respectively. The relative proportion of adsorbed Cd was calculated as the amount of metal adsorbed after 24 hours divided by the amount added. Although the amount of adsorbed Cd differs between the soils a common trend for heavy metal adsorption was observed. This pattern, or adsorption envelope, has been reported previously (Elliott et al., 1986) however the mechanism controlling the adsorption behaviour is not understood (Evans, 1989).

FUTURE WORK

Until very recently, modelling adsorption in soils was done using adsorption isotherms or adsorption kinetics. These approaches, however, do not represent a mechanistic approach to adsorption. Attempts have been made to model colloid surface phenomena by introducing the "surface functional group". These "groups" are charged molecular units on soil surfaces that can form complexes with species in solution and include the hydroxyl groups on metal (hydr)oxides and aluminosilicates and carboxyl groups on insoluble organic matter.

Equilibrium constants for the formation of complexes between Cd and the surface functional groups in the soil will be used in a "surface complexation model" to describe adsorption of Cd. A mechanistic model employing metal speciation and surface complexation data will be used to predict leachate Cd transformation within the soil.

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Table 1 The chemical composition of the Guelph, Muskoka, Leamington and Glanbrook leachates.

	Guelph	Muskoka	Leamington	Glanbrook
pH	7.01	5.44	7.65	7.45
			µg/ml	
Mg^{2+}	525	29	70	540
Ca^{2+}	883	203	169	228
K^{+}	1301	114	483	406
Na^{+}	1109	41	373	580
NH_4^{+}	865	103	360	13
Ni^{2+}	0.52	1.46	0	0
Cd^{2+}	0.05	0.12	0.06	0.03
Cu^{2+}	0	0	0	0
Fe^{3+}	1.11	37.52	0.42	0.22
Mn^{2+}	5.07	6.77	0.01	0
Pb^{2+}	0	0	0	0
Zn^{2+}	0.03	2.67	0.04	0.04
F^{-}	0	0	0	0
Cl^{-}	2464	98	900	1039
NO_3^{-}	0	0	0.34	0
PO_4^{3-}	1.38	0	0	0
SO_4^{2-}	49	0	10	258
TOC	3774	2446	216	447
			mmho/cm	
EC	9.92	1.42	5.20	4.25

Table 2 Geochem - Muskoka leachate speciation

		pH = 5.44		
		% Bound With		
Metal	% Free Metal	CO_3	Cl	OH
Ca^{2+}	99	0	1	0
Mg^{2+}	99	0	1	0
K^{+}	100	0	0	0
Na^{+}	100	0	0	0
Fe^{3+}	0	0	0	100
Mn^{2+}	100	0	0	0
Cd^{2+}	79	0	21	0
Zn^{2+}	98	2	0	0
Ni^{2+}	96	4	0	0

Table 3 Geochem - Guelph leachate speciation

		pH - 7.01			
		% Bound With			
Metal	% Free Metal	CO_3	Cl	SO_4	OH
Ca^{2+}	80	0	19	1	0
Mg^{2+}	83	0	16	1	0
K^{+}	97	0	3	0	0
Na^{+}	95	0	5	0	0
Fe^{3+}	0	0	0	0	100
Mn^{2+}	92	3	4	1	0
Cd^{2+}	12	0	88	0	0
Zn^{2+}	80	14	4	1	1
Ni^{2+}	67	28	4	1	0

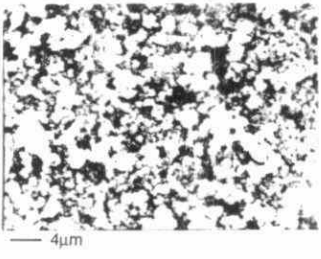

Fig. 1 Scanning electron micrograph of ferrihydrite in the Muskoka leachate.

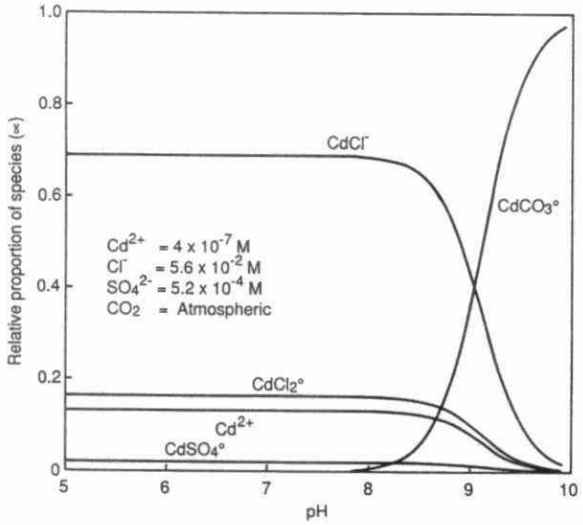

Fig. 2 Distribution of Cd2+ species at different pH values for the Guelph leachate.

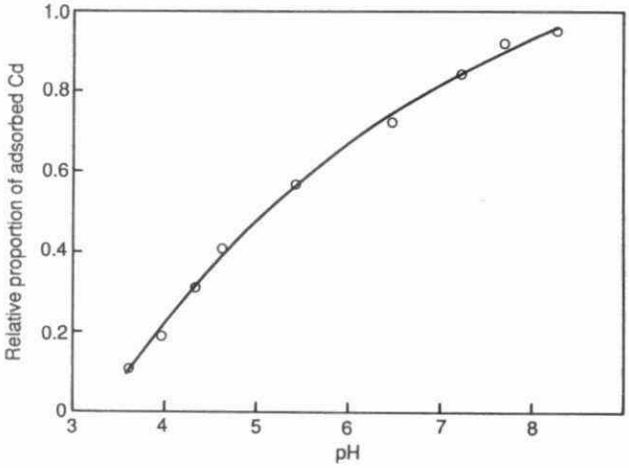

Fig. 3 The pH-dependent adsorption of Cd (0.1 mM) on the Glanbrook Ap soil.

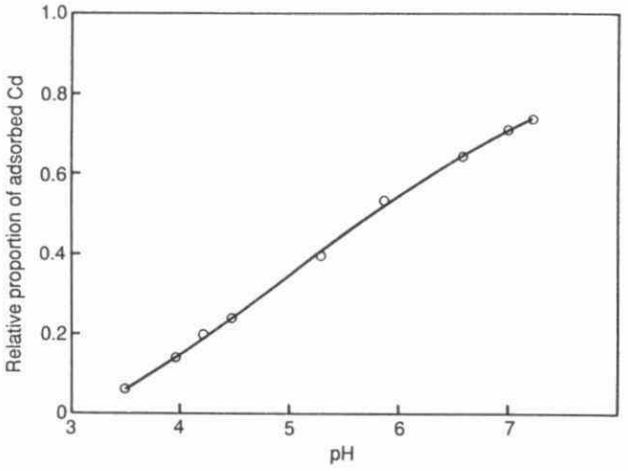

Fig. 4 The pH-dependent adsorption of Cd (0.2 mM) on the Guelph Ap soil.

C13

FISH WASTE PRODUCTION - RAINBOW TROUT CULTURE

P.S. Chisholm P.Eng. and J.B. Farrell B.Sc. (Eng.)*

This study provides new information about quantitative estimates of waste production within land based rainbow trout culture. The estimates are related to fish size, and quantity and quality of feed consumed. Such estimates are required to describe the water quality conditions both within fish culture operations and in the effluent from them.

Knowledge about water quality conditions within fish culture operations is essential for effective waste management in the growth environment. Also, effective management of effluent waste products requires quantitative information about effluent quality.

Estimates of waste production are calculated from a three part empirical model. Fish growth is modelled as a function of time according to water temperature, fish size and environmental parameters that account for the geometry of the holding facility. Given estimates of fish size, and corresponding growth rates, the second part of the model provides an estimate for the quantity of feed consumed by an individual fish on a daily basis. Alternative estimates for daily feed consumption are derived from feed conversion ratios and optimum feed consumption charts.

In the third part of the waste production model, estimates of feed consumed by an individual fish are translated into estimates of the quality of waste produced by an individual fish. Estimates of waste quantities are determined two ways. Based upon empirical digestibility and excretion ratios, waste

*The authors are Associate Professor and graduate student respectively, School of Engineering University of Guelph Guelph, Ontario N1G 2W1.

quantities of protein, carbohydrates (sugar and starch), lipids phosphorous and ash are determined from known composition of feed fed. By this method, total nitrogen, total phosphorous, dissolved phosphorous, ammonia, total suspended, dissolved and settled solids are determined.

Alternatively, separate estimates of dissolved, settled and suspended waste products are determined directly from the bulk quantity of feed fed. These estimates are based upon empirical relationship between the quantity of feed fed and corresponding quantities of waste product produced. This method provides quantitative estimates for ammonia, suspended solids, total settleable plus suspended solids, dissolved phosphorous settleable and suspended phosphorous, dissolved nitrogen settleable and suspended nitrogen.

Both methods for calculation of waste quantities, are based upon waste production by a single fish. Linear extrapolation is assumed for estimating waste production by a sample of fish as they grow. Concentration of waste products is determined according to flow rate through the holding facility.

Modelled estimates and experimental observation of waste production by a laboratory sample of rainbow trout have been developed for the period 89 06 01 to date. During this period average fish mass has increased from 10.1 grams to 220 grams and bio-mass has been maintained at approximately 25 $kg.m^{-3}$ in the test facility. This has been managed by removal of fish in relation to fish growth.

The laboratory design for the study is given on Figure 1. The hinged false bottom (item 9) was designed as a grill with 30 mm square openings through which settleable waste produces would fall. These measures were taken to isolate settled wastes from the fish thereby preventing re-suspension of the settled wastes. Thus representative quantities of suspended solids would be produced and observed.

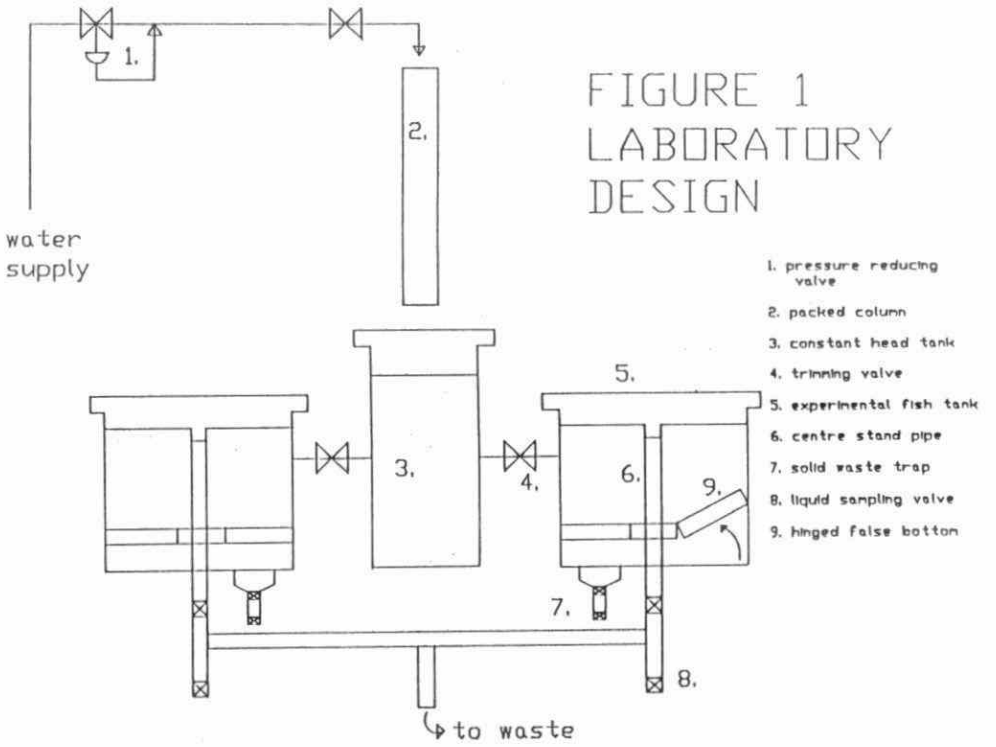

FIGURE 1
LABORATORY DESIGN

1. pressure reducing valve
2. packed column
3. constant head tank
4. trimming valve
5. experimental fish tank
6. centre stand pipe
7. solid waste trap
8. liquid sampling valve
9. hinged false bottom

To date, observed fish growth has been consistent with estimates of fish growth based upon accepted fish growth models for rainbow trout. Also, estimates of the waste products by modelling are consistent with measurements of waste products in the effluent from the experimental tanks.

The modelling and measurement of waste production from this investigation will be completed 89 11 30. Interim experimental results support the following propositions about waste production in land based rainbow trout culture:

- modelling of fish growth in relation to water temperature and geometry of fish holding facilities is feasible;
- modeling of dissolved, suspended and settled solids in relation to fish size and quantity and quality of feed consumed is feasible;
- the concentration of suspended solids in the effluent from the experimental fish rearing tank is consistently less than 5.0 ppm and is directly dependent upon bio-loading;
- the concentration of phosphorous in the effluent from the experimental fish rearing tanks is directly dependent upon the concentration of phosphorous in the feed consumed by the fish.

These propositions will be tested at completion of the investigation when the design implications of the study are assessed.

C14

Manuscript not submitted.

GLASSIFICATION AND LEACHABILITY OF HAZARDOUS WASTES AND HAZARDOUS WASTE RESIDUES. (Project No. 411C) K.B. Harvey*, D.L. Wilkin, and R.J.Porth, Atomic Energy of Canada Limited, Whiteshell Nuclear Research Establishment, Pinawa, Manitoba R0E 1L0.

A consequence of the application of more stringent environmental standards is the need to minimize both the volumes of hazardous materials placed in land disposal sites, and the quantities and levels of hazardous substances subsequently released from them into groundwater. The current work investigates the possibilty of reducing release from hazardous wastes or hazardous waste residues into groundwater by incorporating them into glassy wasteforms. This addresses Environment Ontario Research Need LS12, "Attenuation of Leachate in Groundvater". A simulated waste composition containing all the metals listed in Schedule 4, Regulation 309, has been made. In its raw form it simulates a plating residue, or a dust or sludge from a manufacturing process, or, in its calcined form, an incinerator ash or slag. Wasteforms have been produced by melting 10% or 40% by weight of the waste together with a soda-lime glass composition. Leachate Extraction Procedure Tests at 22.5°C (relating to co-disposal, limited water flov) show reductions of between 3 and 4 orders of magnitude in leachate concentrations for heavy metals, such as As, Cd, and Ba, between the raw waste and the glassy wasteform. Serial leaching of the glassy wasteform (relating to mono-disposal, high water flow) shows heavy metal leachate concentrations below chemical detection limits. These tests are being repeated using radioactive tracers, to improve sensitivity, and at 10°C, as more typical of a subsurface ground temperature. Future studies could include optimization of vasteform composition, and investigation of novel incineration methods that incorporate volume reduction and wasteform production in one process. The latter would address Research Need LS03, "Technology for the Destruction and Disposal of Municipal and Industrial Wastes".

C15

Research and Development of Permanent Onsite Solutions for Clean Up of Groundwater at Waste Disposal and Industrial Sites in Canada - Phase I Update

P. Hannak", B. Whiffin, D. Graham and R. Rush,
CH2M HILL Engineering Ltd. (formerly CANVIRO Consultants),
Suite 600, 180 King St. S, Waterloo, Ontario, N2J 1P8

1. Abstract

This paper describes the accomplishments and future directions of a two-phase project being conducted to develop and demonstrate technologies for remediation of groundwater contamination at waste disposal and industrial sites throughout Canada.

The research and development is focussed on the remediation of contamination due to organic chemicals including phenoxy acid herbicides, aniline, chlorophenolics and volatile organics. The site selected for the demonstration is the Uniroyal Chemical manufacturing plant in Elmira, Ontario.

The project approach uniquely integrates theoretical models used to predict groundwater movement, bench-scale experiments estimating the potential migration and treatability of the contaminants with pilot-scale demonstration at the site.

Phase 1 of the project was completed in mid-1989, the results of which are discussed in this paper.

Phase 1 consisted of:

i) Site and groundwater characterization
ii) Numerical simulation of groundwater flow
iii) Batch tests to estimate sorption of selected target contaminants to soil
iv) Identification of applicable treatment technologies
v) Bench-scale biological and simultaneous biological/powdered activated carbon (PAC) treatability studies

Purging of the contaminated aquifer followed by above ground treatment was identified as a viable technology option. Combinations of biological treatment in a sequential batch reactor and carbon adsorption were selected for the above ground pilot-scale demonstration.

2. Introduction

Although a variety of remediation technologies have been developed to address decontamination of waste disposal sites, the applicability of these technologies to specific site conditions needs to be demonstrated. Furthermore, there is a need to establish a general approach for the evaluation and selection of viable, low cost technologies.

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Definition of the governing methods of process selection, in conjunction with the identification of pertinent site and waste parameters, are expected to assist in the scale up and extrapolation of the results of research and development for other applications.

The appreciation of this need led to the development of an applied research project. Several supporting factors were also considered:

i) Many sites are known to exist in Canada where groundwater contamination by organic chemicals may require addressing in the near future

ii) Removal and offsite disposal of contaminated residues and soil is extremely costly and liability for the waste remains with the generators though the waste is no longer in their control

iii) A review of remediation technologies frequently implemented at hazardous waste sites indicated a limited success due to constraints of the technologies and their applicability

The benefits of such a project thus include:

- Restoration of hazardous waste sites for industrial and public use
- Prevention of further contamination of the neighbouring river, water wells, or other sources of drinking water.
- Guidance for the remediation of additional sites having similar characteristics to the site which is the subject of the demonstration project.

3. Site Selection and Hydrogeology

The site selected for both development and demonstration projects is the Uniroyal chemical manufacturing plant at Elmira, Ontario (hereafter referred to as the Uniroyal site) (see Figure 1). The company was and remains under a Control Order from the Ontario Ministry of the Environment related to environmental impacts arising from its waste disposal. The plant has been in operation since 1942 and has produced a large number of products composed primarily of organic chemicals.

Of particular concern is the water supply aquifer for the Town of Elmira. The water supply aquifer passes beneath the Uniroyal site and municipal water wells for the Town are located at close proximity to Uniroyal (see Figure 2). Chemicals have migrated into the municipal water supply aquifer beneath the site.

Recent concern with toxic organic chemicals in the environment, together with the number of different waste sources at the Uniroyal site and the threat of potential contamination of a potable groundwater supply, make the Uniroyal site ideal and unique for research, development and demonstration (R, D&D) of

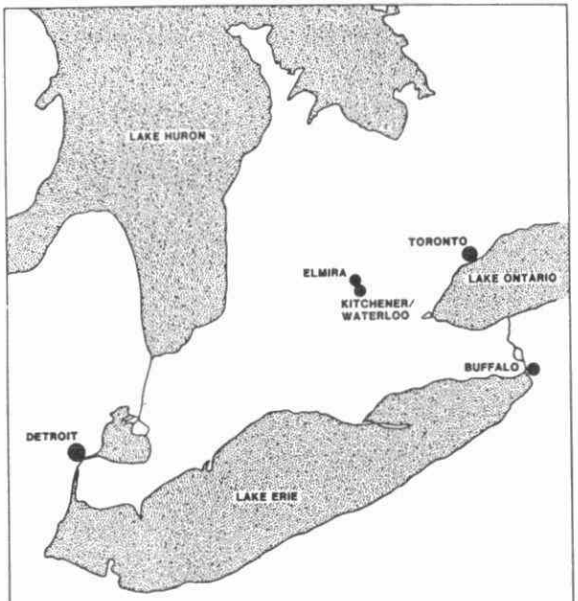


FIGURE 1

LOCATION OF
UNIROYAL CHEMICAL DEMONSTRATION SITE
AT ELMIRA, ONTARIO

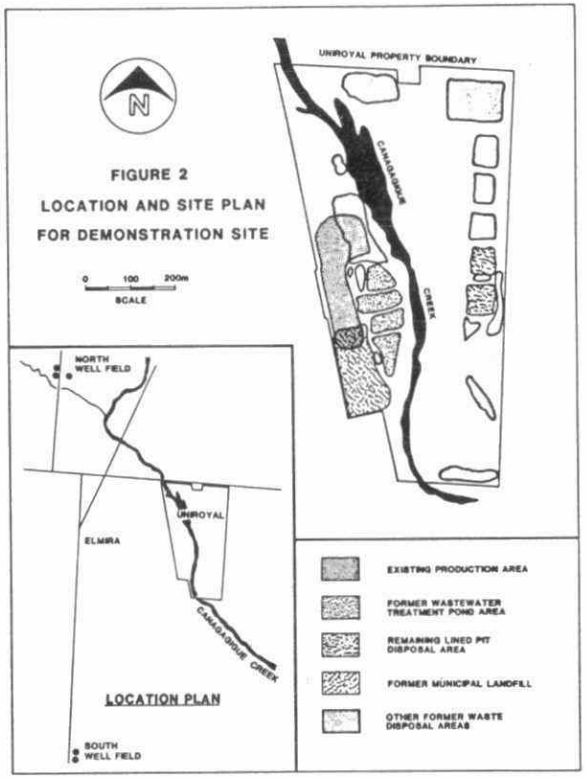


FIGURE 2

LOCATION AND SITE PLAN
FOR DEMONSTRATION SITE

permanent onsite remedial technologies for organic contamination of groundwater at waste disposal or industrial sites.

The geology of the site consists of a complex sequence of glacial, glaciofluvial and glaciolacustrine deposits (Figure 3). Extensive research of the Uniroyal site has been conducted primarily by Morrison Beatty Limited (MBL 1985, 1987, 1988, 1989) as well as Terraqua (1987).

The most significant environmental impact identified by the MBL studies was the contamination of the municipal aquifer beneath the Uniroyal property. Elevated concentrations of a number of groups of organic chemicals were observed at onsite monitoring wells in this aquifer. The potential for these chemicals to reach the municipal wells is of great concern.

Documented hydraulic heads in the surficial aquifer clearly demonstrate that groundwater flow is occurring both laterally towards Canagagigue Creek and vertically downward toward the underlying municipal aquifer (MBL, 1985). Lateral migration has resulted in discharge of contaminants to the adjacent creek. Vertical migration has led to the distribution of toxins in the underlying outwash and till materials. Although previous work on the Uniroyal site has led to elimination of some contaminant sources, others still exist and the contaminants distributed within underlying soils continue to act as a source of contaminants to the deep aquifer. Certainly any remedial work needs to address this situation.

Based on the site hydrogeology and history, the most appropriate area of the site was chosen for the study. The selection factors considered were as follows:

- existence and contribution of known contamination sources
- minimizing the incremental spread of groundwater contamination due to pilot-scale testing
- cost implications to install and operate the pilot demonstration system
- concurrence with Uniroyal's environmental management plans

Through a consideration of all these factors, the former wastewater treatment pond area (see Figure 2) was selected as the preferred site for pilot-scale studies. This area is characterized by high levels of contamination in the municipal aquifer and even higher levels in the shallow aquifer. It became apparent through the course of the preliminary investigation that the shallow aquifer was acting as a source of contamination to underlying strata and that any efforts to restore the municipal aquifer would be futile and unsuccessful without first addressing the shallow contamination source.

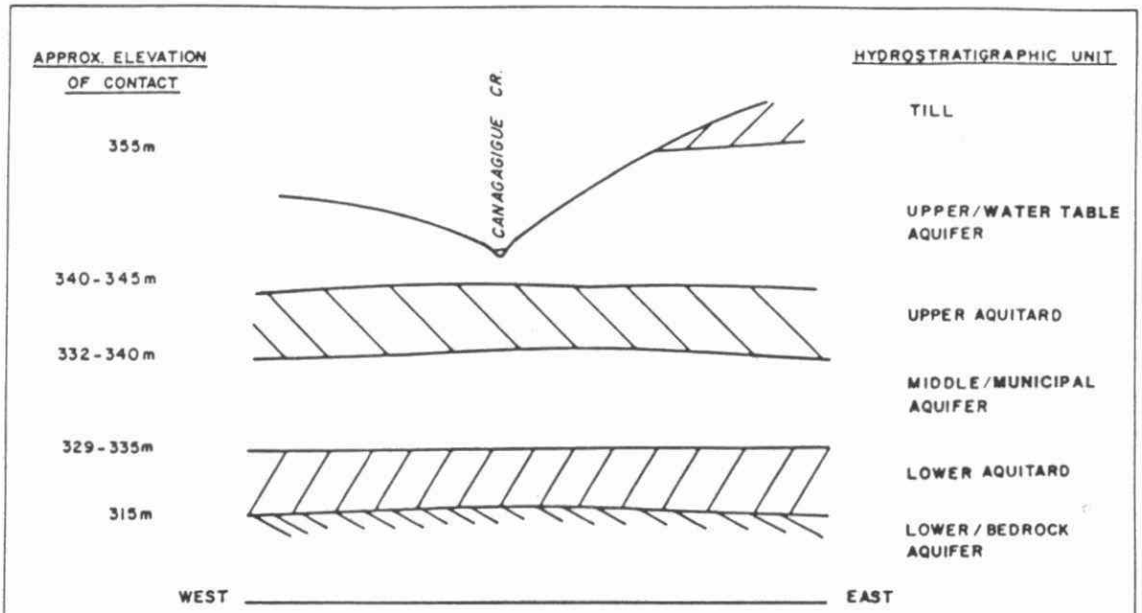


FIGURE 3

GENERALIZED HYDROSTRATIGRAPHY (MBL, 1985)

4. Project Scope and Approach

An integrated but stepwise approach was adapted in the design and execution of the project. CH2M HILL's integrated engineering approach is presented in Figure 4.

Based on the project objectives and site characteristics, a specific project scope was derived.

A short-list of the chemicals of interest was developed (Table 1) based on the materials used in manufacturing and the waste products generated by Uniroyal along with analytical composition of the groundwater in the testing area.

Table 1
CHEMICALS OF INTEREST IN GROUNDWATER AT THE UNIROYAL SITE

Chemicals	Primary	Secondary
Toluene	X	
Benzene		X
m- & p-Xylene		X
o-Xylene		X
Chlorobenzene	X	
2,4-D(2,4-dichlorophenoxyacetic acid)	X	
2,4,5-T(2,4,5-trichlorophenoxyacetic acid)	X	
Phenols		X
Aniline	X	
Nitrobenzene	X	
Mercaptobenzothiozol	X	
Hexachlorobenzene		X
2,3,4-TCP(2,3,4-trichlorophenol		X
2,3,4,5-T_4CP(2,3,4,5-tetrachlorophenol)		X
2,3,4,6-T_4CP(2,3,4,6-tetrachlorophenol)		X
2,4,5-TCP(2,4,5-trichlorophenol)		X
2,4,6-TCP(2,4,6-trichlorophenol)		X
PCP(pentachlorophenol)		X

Efforts are directed to select appropriate criteria for judging the success of the pilot-scale demonstration. However, resolution of this issue has not been achieved to date.

5. Technology Review and Selection

A comprehensive review of existing and emerging remediation technologies was carried out. Technologies screened can be classified into two major groups as follows:

- In situ
- Above ground

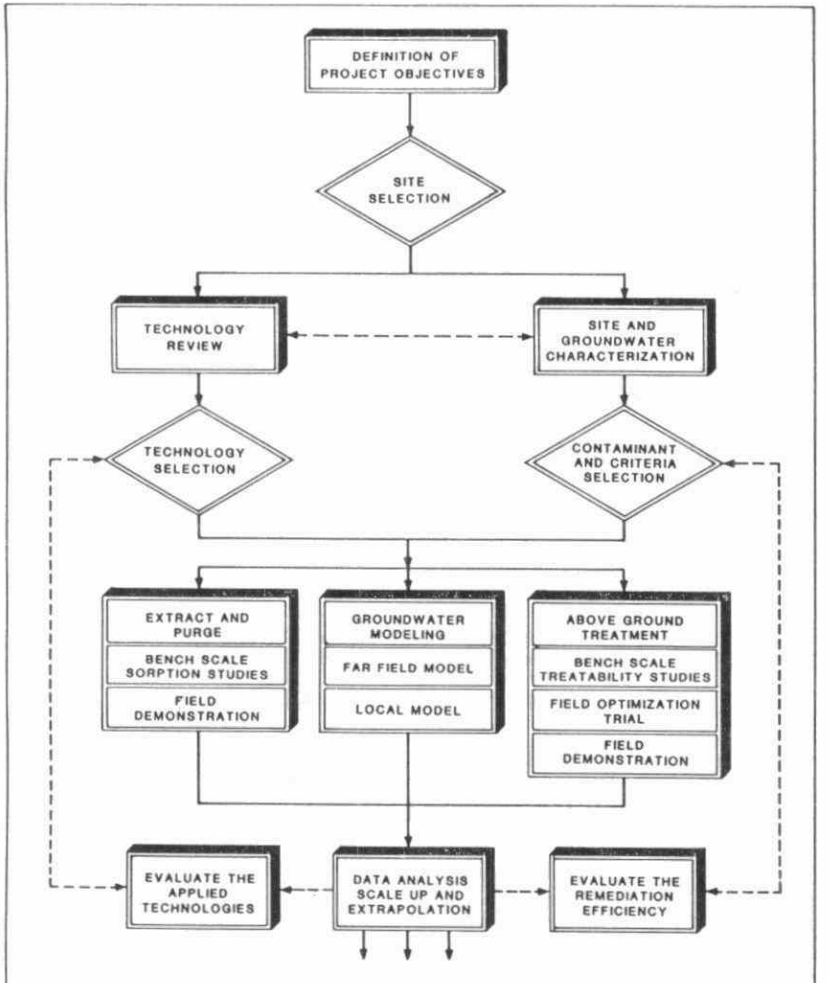


FIGURE 4:
INTEGRATED ENGINEERING APPROACH

CH2MHILL

Sub-groups of these classes include:

- Physical treatment
- Chemical treatment
- Biological treatment
- Air emission control

Through the course of this review, it has become clear that no single technology can address all aspects of a complex remediation task. It was also concluded that several other technologies were not applicable to this particular site.

Out of the in situ treatment technologies, biological remediation and vapour extraction possessed the greatest potential for application at Uniroyal but were eventually ruled out in favour of purge and treat methods for one or more of the following reasons:

- Moderate aquifer hydraulic conductivity (ie. 3×10^{-5} - 3×10^{-3} cm/sec)
- Unknown metabolic pathways and the yield of potentially hazardous by-products during bioremediation
- Neither technology was likely to address all contaminants of concern resulting in residual aquifer contamination

Through an elimination process, purging of the contaminated groundwater followed by above ground treatment were identified as suitable technology options.

Purging can only be efficient if the contaminants are mobile and tend to readily partition into the groundwater rather than retained by the soil. The partitioning may be characterized by the Retardation Factor (R). Therefore, R values of the contaminants of concern were derived. The calculation methods were based on the organic carbon content and typical soil density and porosity of several soils in Ontario (Gillham et al, 1978). Laboratory-scale batch equilibrium adsorption tests were conducted to assess the reliability of empirical estimates of R. It was concluded that the contaminants of interest at Uniroyal were relatively mobile in the subsurface and that purging was applicable for demonstration testing.

The primary above ground treatment technologies which are applicable to the conditions at Uniroyal include:

- Aerobic biodegradation
- Air and steam stripping
- Membrane processes

- Oxidation
- Adsorption (onto activated carbon)

It was decided that the study will focus on the optimization of a selected aerobic biotreatment process followed by carbon adsorption. Membrane processes and oxidation will be evaluated and tested by others.

Figure 5 shows selected process train options.

Sequencing batch reactor was chosen over other biological processes for the following features:

- Capability to equalize shock loadings
- Applicability to a wide concentration range of organics
- Increased and undisturbed settling area
- Single reactor, separate clarifiers and return system are not required
- Flexible operation for low and high rate discharges and for nitrification and denitrification control
- Powdered Activated Carbon adsorption may be combined with the biological treatment

Laboratory Testing

Laboratory testing was carried out to:

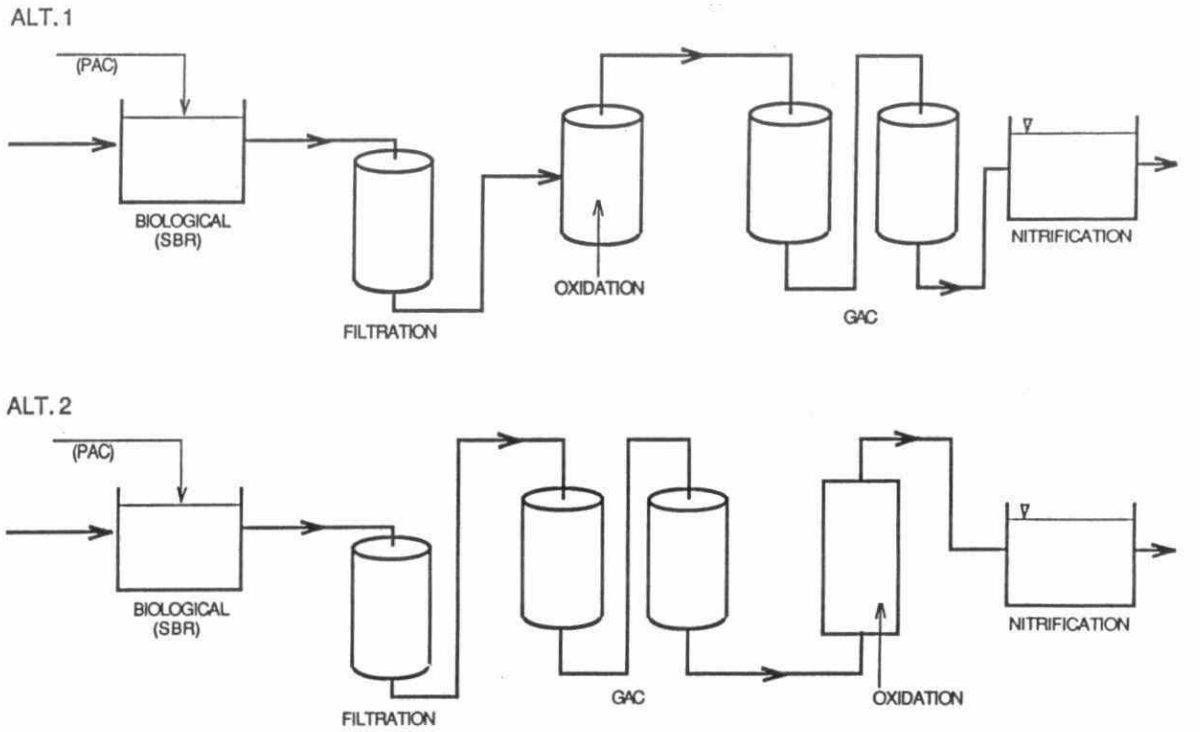
- demonstrate treatability of the groundwater
- provide information on the partitioning of contaminants for purging

1) Bench-scale treatability studies

The objectives of these studies included:

- Verification of the treatability of groundwater samples representing variances in the groundwater composition
- Establishing a range for achievable removal rates
- Identification of specific compounds amenable to the treatment
- Identification of major recalcitrant contaminants for further treatment
- Derivation of information for process selection and design

FIGURE 5. TREATMENT PROCESS TRAIN DESIGN OPTIONS



A batch type treatment study was carried out in two phases with and without the addition of Powdered Activated Carbon (PAC).

Mixed liquor from the Elmira sewage treatment plant (STP) was used as the source of a suitable seed for the treatment. The mixed liquor was acclimated prior to the treatment with increasing concentration of groundwater.

Figure 6 shows reduction of Dissolved Organic Carbon content (DOC) as a function of treatment time. Additional experiments are underway with the combination of Bio and PAC treatments. A more detailed discussion on the treatment experiments is given in the Phase 1 (CH2M HILL, 1989) report.

Additional sorption tests are also planned to evaluate the potential of Granular Activated Carbon adsorption and to also select compounds to be monitored in the demonstration phase.

2) Bench-scale soil sorption studies

Sorption is believed to be the primary process affecting contaminant mobility, therefore efforts are concentrated on this process.

The testing in progress consists of two primary components:

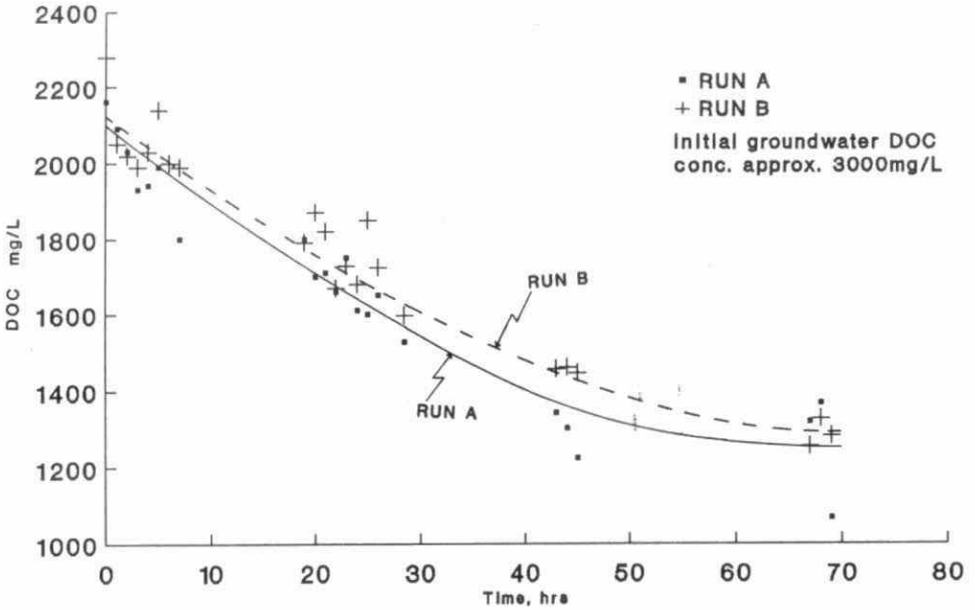
- Laboratory-scale adsorption tests
- Laboratory-scale desorption tests

(i) Laboratory-Scale Adsorption Tests

Laboratory-scale tests are being used to assess adsorption under equilibrium conditions. The advantages and disadvantages of these tests are described in Gillham et al (1987). Key aspects of the methodology are summarized below:

- Sorption is inferred based on solute concentration prior to and following equilibration with clean porous media from the Uniroyal site
- Solution concentrations span the range of groundwater concentrations observed at Uniroyal
- Adsorption is assessed under single contaminant (ie. benzene only) and multi-contaminant (ie. toluene, chlorobenzene, 2,4-D, 2,4,5-T, benzene, m- & p-xylene and o-xylene) conditions to assess competitive and/or co-solvent effects
- The sensitivity of adsorption to other contaminants present at elevated concentrations in groundwater at the site is assessed by conducting tests with/without the contaminant aniline
- Tests are performed under typical in situ groundwater conditions (ie. 10°C, darkness)

FIGURE 6: DOC vs TIME FOR BIOLOGICAL TREATABILITY TEST FOR OW-54-5



- Equilibration occurs over a period of 3 days which has been found to be sufficient by other researchers (Curtis et al, 1986)

- Interpretation of results includes extensive QA/QC to account for variation inherent in any analytical methods, losses during the tests, raw water contamination and soil heterogeneities

The results of this work will be compared to the adsorption predicted by empirical methods to assess whether empirical methods provide a suitable estimate of adsorption in a multi-contaminant environment such as that at Uniroyal. If empirical methods prove sufficiently reliable, laboratory adsorption tests would not be required to quantify adsorption at other similar sites.

(ii) Laboratory-Scale Desorption Tests

Desorption tests are being conducted under dynamic conditions by desorption from contaminated aquifer material in laboratory columns. The objectives of these experiments are:

- To determine the relationship between the volume of uncontaminated water flushed through a soil and the aqueous concentration of the effluent

- To determine the dependence of (i) on velocities likely to be encountered under natural and induced (ie. pumping) gradient conditions

- To compare the results to estimates based on empirical correlations, equilibrium adsorption tests and field scale injection/withdrawal extraction tests (discussed subsequently)

- To examine mathematical models to characterize desorption processes including kinetic effects (if necessary)

Desorption tests will be used to evaluate the desorption behaviour of several contaminants of concern at Uniroyal as well as to assess the applicability of these tests as a predictive tool. Results will be compared to the results of field scale testing described subsequently.

7. Groundwater Modelling - Development of an Aquifer Restoration Management Model

The intent of this component of the approach is to couple the results of lab and field scale demonstrations specific to both treatment and purging processes. These results would then be used to extrapolate to full scale aquifer restoration at the site.

It is planned to investigate methods to optimize aquifer restoration including both formal (ie. linear and/or non-linear programming) and informal approaches (ie. ad-hoc approach based on scientific judgment). At present, the heterogenei-

ties at the site such as numerous waste sources and variable hydrogeology suggest that more formal approaches are not applicable.

To date, a model has been developed to simulate groundwater flow at a regional and at a local scale in 3-D. A regional scale model was developed first to:

- determine if sufficient hydrogeological information existed to reproduce measured hydrogeologic conditions,
- develop a better understanding of the regional and local hydrogeology, and
- assist in developing boundary conditions for the local scale model including the effects of municipal well pumping.

Once the regional model is calibrated, a local scale model will be developed to simulate the affect of various pumping schemes in achieving aquifer restoration.

8. Future Tasks

In addition to the completion of bench-scale studies and groundwater modelling work, three major field tasks will be carried out in the continuation of the project (Phase 2):

- Field-scale injection/withdrawal extraction test
- Optimization of the treatment process
- Demonstration of the treatment process

A final report is expected to relate to the results to other groundwater contamination problems wherever possible.

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Acknowledgements

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C16

EFFICACY OF ELECTROCHEMICAL TREATMENT IN REMOVING COLOUR FROM, AND REDUCING TOXICITY OF, TEXTILE DYEBATH EFFLUENT

A.E. Wilcock* and M.C. Boreskie
University of Guelph, Guelph, Ontario N1G 2W1

ABSTRACT

This research was designed to test the efficacy of a new, commercially available electrochemical cell in the purification of environmentally hazardous textile dyebath effluents. These effluents contain expensive dyes and other chemicals which, if they can be reclaimed, represent a substantial economic saving. More importantly, reduction of the chemical content and toxicity of the used dye liquors will provide the textile industry with the choice of either safely dumping the purified water-like effluent or recycling it in subsequent dyeing cycles.

The treatment has been applied to three of the most commonly-used disperse (polyester) dyes in Ontario. It was highly effective in colour removal and in reducing the toxicity of the effluents as determined by Daphnia magna bioassay. Subsequent use of the purified effluent produced high quality dyeings although the colour differences between the samples dyed using initial and recycled liquor were greater than recommended tolerances.

The electrochemically treated effluent contained substantial amounts of iron, a problem if it were reused in conjunction with metal-sensitive dyestuffs. Reuse of the dyes recovered from the effluent has not yet been investigated.

INTRODUCTION

During recent years, environmental issues have become the focus of public attention. A major concern has been pollution of the environment as a result of various manufacturing industries, including textiles (6, 11, 12, 14). Effluent from textile dyebaths, in particular, are not only aesthetic pollutants by virtue of their colour, but may impede light penetration in the receiving body of water, thus interfering with biological processes (7). Dye effluents also pose the problem of potentially toxic or carcinogenic chemicals entering sewage treatment facilities not specifically designed for them (17).

Conventional biological treatment of dye effluents has not been particularly effective as many dyestuffs are resistant to degradation (4, 5, 15). Such treatment has also been reported to be particularly ineffective in removing colour from dye effluents (10).

Although several physical and chemical methods have been used to treat dye effluent, no one treatment seems suitable for all dye effluents. Rather, the effectiveness of each is dependent upon the type of dyestuff and chemical assistants used for dyeing (7). Carbon adsorption and ozonation have been shown (16) to be ineffective in colour removal from disperse dyebaths whereas both chemical coagulation and reverse osmosis are highly effective. Unfortunately, reverse osmosis involves high capital costs.

Electrochemical methods have been used in several ways for the treatment of effluents. The skim tank of a typical biological waste treatment system has been designed as a basic electric cell to assist in suspended solids removal (1). An electrolytic cell has been used in the production of hypochlorite in the treatment of wastewater (8). Electrochemical treatment has also been used as one component of a five step procedure in processing dyebath effluent (3).

An electrochemical method has recently been developed by Andco Environmental Processes Inc. (Amherst, N.Y.) for the removal of heavy metals from wastewater. The method, which is based upon the use of sacrificial iron electrodes, has also been shown to be a simple and effective means of removing selected dyes from effluents (9, 2, 18). This paper is a report of preliminary results of an ongoing study involving the use of the Andco process in the purification and recycling of disperse (polyester) dye effluents.

MATERIALS AND METHODS

Materials

1. Dyes:
The sales managers of five large dye suppliers were contacted for data on the most commonly used disperse dyes in Ontario. The two most popular reds, blues and yellows were screened for their environmental toxicity (as described below) and the more toxic of each color was used. Those three dyes were C.I. Disperse Blue 56, C.I. Disperse Red 60 and C.I. Disperse Yellow 34.

2. Fabric:
One hundred percent Dacron polyester was used as the substrate to which the dyes were applied.

Methods

1. Electrochemical Treatment:

The system used in this study was a laboratory-scale electrochemical cell obtained from Andco Environmental Processes, Amherst, N.Y. Wastewater was circulated around two iron electrodes to which an electric current was applied. Iron was released from the anode, with the following reaction occurring:

Anode (oxidation):

$$Fe \quad --- > \quad Fe^{++} + 2e^-$$

Cathode (reduction):

$$2H_2O + 2e^- \quad --- > \quad H_2 + 2OH^-$$

Overall Reaction:

$$Fe + 2H_2O + \text{Electrical Energy} \quad ---> \quad Fe(OH)_2 + H_2$$

The freshly-produced iron hydroxide facilitated adsorption of the dye from the effluent.

Prior to passage through the cell, the pH of the liquor was lowered to approximately 3.0. The cell was operated at 0.4 amperes for eight minutes in order to release sufficient iron to optimize removal of the residual dyestuff from the effluent. After passage through the cell, the pH was raised to 8.5 and polyacrylamide polymer added to stimulate flocculation and precipitation of the iron hydroxide and adsorbed dyestuff. The treated dyebath was then filtered (Whatman #2) with suction.

Visible spectra were produced for each of the three dye effluents before and after electrochemical treatment (Hewlett Packard 8451A Diode Array spectrophotometer, Palo Alto, Cal.). Since disperse dyes are virtually insoluble in water, an organic solvent (acetone) was used to dissolve them prior to spectral analysis. For each sample, the ratio of acetone to deionized water (plus constituents) was 9:1.

2. Dyeing and Colour Measurement:

The dyebath formulation was that recommended by the Dyestuff & Chemical Division of Ciba-Geigy Corporation (Greensboro, N.C.) and is as follows:

Disperse dyestuff, X%
Tinegal NT, 0.5%
Sodium acetate, 2.0%
Acetic acid (56%), 1.0%
Dyebath:Fabric weight, 15:1
pH, 4.5-5.0

A 1% dyeing (based on fabric weight) was used because it did not result in a large amount of residual colour in the bath after dyeing. Deionized water was used for the purposes of laboratory control.

Each specimen of polyester fabric weighed 10 ± 0.20 grams. Four specimens were dyed with each dye. The fabric swatches were initially saturated with deionized water containing a few drops of Triton X-100 (Rohm & Haas, Philadelphia, Pa.). Dyeing was done in a rotary laboratory dyeing machine (Atlas Launder-Ometer, Atlas Electric Devices Co., Chicago, Ill.), beginning at a temperature of approximately 55C. The temperature was raised to the boil over 30 minutes. The temperature was maintained at the boil for 45 minutes and then lowered to 78C. The samples were removed from the dyebath, rinsed in hot (49-54C) deionized water and then dried at room temperature. The used dyebath and rinse water were combined and 1 liter was passed through the electrochemical cell and filtered.

The filtered effluent was used to formulate a new dyebath within 96 hours following filtration. This reconstituted dyebath had the same formulation as the initial dyebath except that the recycled effluent was used instead of deionized water. The pH was lowered to equal that of the initial dyebath (4.5-5.0) and the dyeing was performed as before.

For each dyestuff, the colour of the specimens which had been dyed using the fresh and recycled liquor was compared. Five colour measurements were done on each specimen using a ColorQUEST spectrocolorimeter (Hunter Associates Laboratory, Reston, Va.).

3. Toxicity Tests:

The toxicity of the samples to Daphnia magna was assessed following the protocol of the Ontario Ministry of the Environment (13) for an LC_{50} for 48 hours. The test was performed on each of the three dyes and Tinegal assistant before dyeing, and on each of the three dyebaths, the Tinegal and water control after electrochemical separation.

RESULTS AND DISCUSSION

1. Electrochemical Treatment:

The visible spectra of the three dye effluents before and after treatment (Figures 1-3) indicate complete extraction of the dyes by the electrochemical method. The single large peak appearing in each of the spectra of the untreated effluents is caused by the dyestuff. The absence of these peaks in the spectra of the treated effluents indicates complete removal of the dyes. A control showed that the peak appearing at approximately 325 nm is caused by the Tinegal NT dyebath assistant in the effluent. The peaks in the 300 nm range are due to noise from the machine.

2. Dyeing and Colour Measurement:

The electrochemically treated, filtered effluent which was used for the final dyeings appeared to contain a substantial amount of iron but no dyestuff. Despite the presence of the iron, the specimens dyed with each of the three dyes in the recycled effluent were as uniform as the controls dyed using deionized water.

The difference in the colour among the replicate control specimens was less than that among the final dyed specimens. It is logical to assume that the colour variation among the latter specimens is due to the presence of the iron in the dyebath.

The red and yellow specimens dyed with the recycled liquor were darker and slightly more red than the controls. The blue samples dyed with the recycled liquor were lighter and more yellow than the controls, probably due to the presence of iron in the effluent. The colour difference between the control and final samples for all three dyes was greater than the recommended 0.50 tolerance level (20).

3. Toxicity of Effluent to Daphnia Magna:

The acute toxicities of C.I. Disperse Blue 56 and C.I. Disperse Yellow 34 were markedly reduced following electrochemical treatment (Table 1-2). To determine toxicity, both the LC_{50} and EC_{50} must be considered. The LC_{50} measures the concentration required to kill 50% of test organisms whereas the EC_{50} measures the concentration required to kill or immobilize 50% of the test organisms. The latter, therefore, presents a more sensitive measure of sample toxicity. It is on the basis of EC_{50} that C.I. Disperse Yellow 34 is considered more toxic before than after electrochemical treatment.

The toxicity of C.I. Disperse Red 60 apparently increased following electrochemical treatment but this result is deceptive owing to the original conductivity of the liquor. Daphnia magna are hard water organisms and cannot survive in solutions that have a low conductivity (19) such as that of C.I. Disperse Red 60 (Table 3). The protocol specifies that tap water be added to the solution and this raised the conductivity of the sample, thereby permitting survival of the organisms. Consequently, the results of the Daphnia magna test for this dyestuff are considered misleading.

Dilution of the solutions had a differential effect on their toxicity. A 50% dilution of the treated blue and yellow dye effluents decreased the mortality of the daphnia by more than 50% whereas a 50% dilution of the treated red dye effluent reduced the mortality by only 25%.

CONCLUSIONS

Electrochemical treatment with iron electrodes was very effective in the removal of colour from C.I. Disperse Blue 56, C.I. Disperse Red 60 and C.I. Disperse Yellow 34. Reuse of the treated effluent resulted in uniform dyeings with no dyespots. The colour differences between initial dyeings and those based on the purified liquor were greater than recommended tolerances. Toxicity of the effluent was substantially reduced by electrochemical treatment in all trials except that with C.I. Disperse Red 60.

The presence of the iron in the treated effluent may contribute to both its toxicity and the colour differences between initial and final dyeings. Furthermore, if metal-sensitive dyestuffs were to be used, the iron could lead to the problem of dyespots on fabrics dyed using the purified liquor.

A few obstacles must be overcome prior to applying this technology to industry. The iron remaining in the treated effluent should be eliminated. Methods to adjust the conductivity of the liquor other than pH must be investigated so that the risk involved in handling substantial amounts of acid and alkali be minimized. (We are currently examining methods to do this.) The frequent use of a sequestering agent in commercial dyeing would necessitate an increase in the amount of iron added to the effluent during treatment. Finally, the disposal of sludge remaining after filtration must be considered until a method can be found for recycling it.

Electrochemical treatment of dye effluent to remove colour and reduce toxicity shows great promise once the attendent difficulties can be overcome.

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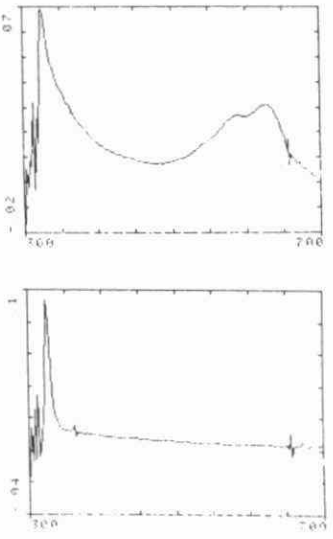

Figure 1. Visbile Spectra of C.I. Disperse Blue 56 (a) Before and (b) After Electrochemical Treatment

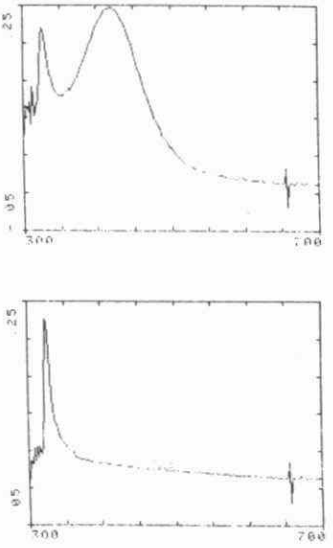

Figure 2. Visible Spectra of C.I. Disperse Red 60 (a) Before and (b) After Electrochemical Treatment

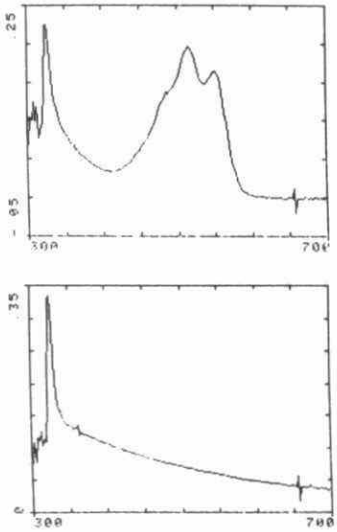

Figure 3. Visible Spectra of C.I. Disperse Yellow 34 (a) Before and (b) After Electrochemical Treatment

TABLE 1. LC50 of Dyes and Assistants to Daphnia Magna

Sample	LC50 (%) Untreated Liquor	LC50 (%) Treated[1] Liquor
C.I. Disperse Blue 56	35.4	60.9
C.I. Disperse Red 60	70.7	24.6
C.I. Disperse Yellow 34	65.8	54.4
Tinegal NT	1.4	10.2
Deionized water control	N.D.[2]	31.9

[1] Treatment consisted of passage through the electrochemical cell followed by filtration.
[2] N.D. = not done.

TABLE 2. EC50 of Dyes and Assistants to Daphnia Magna

Sample	EC50 (%) Untreated Liquor	EC50 (%) Treated[1] Liquor
C.I. Disperse Blue 56	24.0	56.8
C.I. Disperse Red 60	70.7	19.5
C.I. Disperse Yellow 34	32.4	54.4
Tinegal NT	1.4	10.2
Deionized water control	N.D.[2]	31.9

[1] Treatment consisted of passage through the electrochemical cell followed by filtration.
[2] N.D. = not done.

TABLE 3. Conductivity of Dyes and Assistants Before and After Electrochemical Treatment

Sample	Conductivity Before Treatment	Conductivity After Treatment
C.I. Disperse Blue 56	259	3114
C.I. Disperse Red 60	61	1465
C.I. Disperse Yellow 34	290	2560
Tinegal NT	254	987
Deionized water control	N.D.[1]	2130

[1] N.D. = not done.

C17

DRAFT
ASSESSMENT OF THE CURRENT WASTE MANAGEMENT PRACTICES ON FARM OPERATIONS IN PERTH COUNTY ONTARIO

by

Murray Haight
Paul Cahill

School of Urban and Regional Planning
University of Waterloo
Waterloo, Ontario N2L 3G1

Problem Statement

In recent years the management of wastes from various sources has been a concern of governments, industry and the public. While increased volumes of waste from urban and rural areas have put pressure on existing landfill spaces, wastes from farm operations, not including farm livestock related wastes, have not been addressed to any great extent. In 1983, the Ontario Ministry of the Environment (MOE) released a "Blueprint for Waste Management" (MOE, 1983). The report outlined some principles for waste management; but, agricultural wastes were not dealt with specifically. In 1985, the Environmental Protection Act (EPA) (MOE, 1982) was amended with the addition of Regulation 309 (MOE, 1985), to assist in the management of wastes in Ontario. Under Regulation 309, section 3, subsection 1, "Agricultural Wastes" are exempt from Part V of the EPA and Regulation 309. In Regulation 309 agricultural waste is however defined as "...waste, other than sewage, resulting from farm operations...". This definition could include such wastes as empty pesticide containers, empty fertilizer containers, farm machinery wastes and farm household wastes.

MOE is currently addressing waste management from industrial and municipal sources under the Municipal/Industrial Strategy for Abatement (MISA) program (MOE, 1988). Under this program, household hazardous wastes have been identified as a potential environmental problem; however, again farm hazardous wastes remain to be addressed. The Ontario Ministry of Agriculture and Food (OMAF) have produced "factsheets" to assist in the handling and disposal of potentially hazardous wastes such as pesticides and empty pesticide containers (Frank and Ripley, 1988: Frank and Winfield, 1987, 1986a; Frank and Chisholm, 1986b; Wolfe et al, 1961). It has been suggested that the triple rinsing of "empty" pesticide containers, puncturing them to render them useless and burying them at least 50 cm deep is an acceptable form of disposal. A study by Miles et al (1983) found that less than .1% of the original contents remained in either triple rinsed containers or jet rinsed containers. In 1988, the Crop Protection Institute of Canada formed a Task Force on Crop Protection Chemicals in Water (Sawyer, 1989). The main purpose of this task force was to help eliminate human error in handling pesticides and reduce the amount of pesticides reaching surface waters. A pamphlet was produced called "Water in Trust", which emphasized the need to protect the environment from pesticide contaminants (CPIC, Undated). Triple rinsing "empty" pesticide containers was noted as a necessary practice to decrease the potential for contamination.

Within the last couple of years, farm organizations, chemical manufacturers and governments have been attempting to address the problem of container disposal with alternative packaging, deposits on containers and special waste dumping

days (Rude,1989; Sawyer, 1989). A study has been conducted at the University of Guelph, that examined the potential for recycling plastic pesticide containers with regard for potential chemical contamination of the plastic (Sawyer, 1989; Rude, 1989). Used pesticide drums have also been targeted for recycling in some areas of Ontario (Ford, 1988).

The quantities of active ingredients of pesticides used in Ontario on major field crops, fruits and vegetables and roadsides, increased by 32% to 8.8 million kilograms of active ingredients between 1978 and 1983, with a corresponding increase in the area sprayed of only 2.6% (from Roller, 1979; McGee, 1984). Approximately 60% of farm pesticides are distributed in plastic containers (Rude, 1989). Machinery wastes from farm operations have not been addressed as being a potential pollution problem. Census farms reported in Ontario in 1986, having a total of 79,228 trucks, 187,165 tractors and a combined 85,953 grain combines, swathers, balers and harvesters (OMAF, 1987). Assuming 20 liters of waste oil could come from each piece of equipment in a year, this would result in about 7 million liters of waste oil from farm operations in Ontario per year.

There has been relatively very little research reported on total farm waste management which would include waste pesticide containers, waste fertilizer materials, wastes from farm machinery, household and yard wastes and other wastes that may be present on farm operations. A review of literature has not uncovered any survey reports of the overall disposal practices of farm operations.

Project Objectives

The main goals of this study were to determine the types and quantities of wastes being generated by farm operations in Perth County, Ontario and to assess the general current waste management practices.
Specific objectives included:
- to identify the nature of wastes generated
- to identify the quantities of each type of waste
- to examine the existing disposal practices
- to estimate the potential environmental impacts as a result of the current waste management practices identified
- to survey the opinion of farm operators regarding alternatives to current waste management practices arising from other farm operations throughout the Province.

Research Procedure

Data collected for this study was obtained from a literature review conducted at local libraries, personal communications with external agencies (Hanly, 1988; Harris, 1988; Blackie, 1989; McGee, 1989; Sawyer, 1989) and from personal interviews of randomly selected farm operations in

Perth County, Ontario. The survey data was collected from a personally administered questionnaire. The questionnaire was developed to collect data on the types and quantities of wastes being generated and the current disposal methods. Farm operator opinions regarding practical alternatives were also surveyed. The format of the questionnaire included questions to collect data on the types and quantities of wastes generated and the current disposal methods. Five general waste types were include on the questionnaire: pesticides related, fertilizers related, machinery related, house and yard related and other wastes. Pesticide and fertilizer related waste were assessed by crop type. Much of the data sought was directed towards the areas of empty pesticide container disposal and the potential for ground water contamination.

The questionnaire also collected data that could be compared with other survey data such as the 1986 Agricultural Census (OMAF, 1987) regarding farm types and sizes, and the Survey of Pesticide Use in Ontario (Roller, 1974, 1979; McGee, 1984). Other questions related specifically to pesticide handling locations as they pertained to the drinking water well for the household (Frank and Ripley, 1988). The use of the triple rinsing method of cleaning empty pesticide containers prior to disposal as recommended by government agencies was assessed (Frank and Winfield, 1987c; Health and Welfare Canada, 1986; Miles et al, 1983). Data was also collected regarding well types (drilled or dug), and fuel storage tank locations relative to wells. Finally, farm operators were asked if they perceived any problems with their current waste management practices and if so, what they thought were practical and feasible alternatives. Other data pertaining to the current waste management practices of their home townships was also collected. For example, was there a "blue box" program currently operating in the township.

Farm operations to be surveyed were selected randomly and were stratified to reflect the proportion of farm types present in the 1986 Perth County survey (OMAF, 1987) and to cover all townships within the county. During the distribution of the cover letter an attempt was made to distribute according to the above mentioned proportions. For example, one could usually identify a dairy operation by the presence of dairy cows or a milkhouse. This attempt to stratify the sample was based on the premise that certain farm types would have different crop types, and thus produce different wastes.

A cover letter was developed explaining the objectives of the project, provide some background on the investigator and to inform people about the topic prior to the personal survey. The personal surveys took approximately one half hour to one hour to complete upon contacting the farm operator.

Summary of Findings

The findings of this study are based largely on the data collected from the survey questionnaire. The survey population represented roughly 1% of the 1986 Perth County Census farm population (OMAF, 1987). From the 1986 census farm data, Perth County reported having 2833 census farms. Census farms were defined as having $250 or more in annual sales in agricultural products. It was assumed that the survey population met this criteria based on the fact that all survey farms apparently were full time farm operations. Twenty seven of 87 questionnaires were completed at various times between February and September 1989. The locations where questionnaires were not completed the first visit were revisited up to 3 times to contact someone to complete the survey questions. This method proved to be inefficient due to the lack of set meeting times and the varying schedules of farm operators. An attempt was made to stratify the survey population by the type of farm as discussed in the Research Procedure. The distribution of farm types for the survey population and Perth County 1986 census farm population is listed in Table 1. The 1986 Perth County population had a more even distribution of dairy (26%), hog (23%) and cash crop (29%) operations compared to the survey population which had a distribution of 41%, 22% and 19% respectively.

Waste quantity data was collected for annual production of pesticide, fertilizer and machinery related wastes (Table 2). These quantities represented estimates from the farm operations since they did not refer specifically to written records of ie. pesticide use. The pesticide wastes were divided into two main categories; plastic liquid containers with 5 and 10 litre sizes; and bag type containers for granular materials in less than 5 kilogram and 25 kilogram sizes. These sizes represented the most frequently encountered sizes while the few odd sizes were fit into the closest category. Table 2 includes the response rate of operators producing that waste type and the average quantity produced by farm type. The total survey data showed that 78% of surveyed farm operations produced 10 litre size pesticide container wastes. The majority or 78% of farm operations surveyed reported applying their own pesticides. There were only 22% of all survey farms reporting waste plastic bags related to fertilizers. About 67% of the farms reported using bulk fertilizer applications which could account for the small percentage of farms reporting fertilizer related wastes. Machinery related wastes were the most frequently reported waste type from the survey. An average of 141 litres/year of waste oils were recorded for the 96% reporting producing this waste type. As well, an average of 10 waste oil filters/year and 2 waste batteries/year were reported. Machinery wastes are possibly more related to the size of the farm operations than the type of farm operation. Household

and yard wastes were difficult to quantify and are not reported here.

Waste disposal practices were divided into five types; burn, store, landfill, recycle and reuse on the farm. Table 3 outlines the current waste disposal methods reported by farm operators for pesticide, fertilizer and machinery related wastes. Sixty percent of survey farm operations reported burning their waste pesticide containers, 39% reported landfilling and 1% reported reusing the containers. Almost all (98%) of operations reported burning plastic fertilizer bags. Eighty percent of operations reported reusing waste oil. At first glance this practice would seem ideal; however, these oils were reused on the farm almost exclusively for lubricating machinery/barn equipment or dust suppression on farm roadways. Another 15% of waste oil was burned and the remaining 5% was reportedly stored for future disposal. About 92% of waste oil filters were landfilled and 8% were burned. A majority of the waste batteries (59%) were reported being recycled usually at a service facility off of the farm and 37% reported storing the batteries for future disposal.

Table 4 summarizes the pesticide container rinsing practices of farm operations applying their own pesticides. A total of 10% reported 0 rinses prior to disposal, another 10% reported 1 rinse, 43% reported rinsing twice, 29% reported rinsing 3 or more times and 10% reported rinsing until "clean". A combined total of over 60% reported rinsing their pesticide containers less than 3 times prior to disposal. Almost all of the operators poured the rinsate back into the spray tanks to be applied to the field/crop.

A comparison of 21 of 27 survey farms crop type and acreage data and the 1986 Perth County crop type and acreage data is outlined in Table 5. Ninety percent of the survey reported growing corn (silage or grain) while 86% of the 1986 Perth census farm population also reported growing corn (silage or grain). As well, the 1983 Survey of Pesticide Use in Ontario (Mcgee, 1984) reported that 43% of agricultural pesticides used in Ontario in 1983 were used on corn crops. About 38% of the crop acreage from the 21 farms reporting was reportedly grown in corn compared to 31 % from the 1986 Perth County survey (from OMAF, 1987). About 78% of the pesticide related waste from the survey was related to corn production. Although some of the external data presented for comparison is from different years, it is presented to show general trends and point out possible problem areas.

Some potential environmental impacts relating to the reported waste management practices of the farm operators could include; concerns about groundwater contamination from concentrated pesticide residues in plastic containers burned close to domestic or livestock wells; concerns about the 80 % of waste oil reportedly reused on the farm that ends up in the local environment. Further considerations should be given to pesticide handling, use and container disposal and the resulting impacts on surface waters and groundwater.

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TABLE 1 A Comparision of the Survey Farm Types to the 1986 Perth County Census (from OMAF, 1987)

Farm Type	Survey Population	% Survey Population	Perth Co. Population	% Perth Population
Dairy	11	40	742	26
Hogs	6	22	650	23
Cash Crop	5	19	826	29
Cattle	4	15	513	18
Poultry	1	4	75	3
Other	0	0	27	1
TOTALS	**27**	**99**	**2833**	**100**

Note: Cash crop includes mixed grain operations for both survey and Perth Census populations.

TABLE 2 Percentage of Surveyed Farm Operations Reporting Wastes by Type and Average Annual Quantity.

Farm Type	Sizes/ Units >>	Pesticide Related Wastes: Plastic Cont. 5 l.	Plastic Cont. 10 l.	Bags <5kg	Bags 20kg	Fertilizer Rel. Wastes: Bags 25kg	Machinery Rel. Wastes: Oils l.	Filt. #	Batt. #
Dairy	% Resp.	9	64	18	27	45	100	100	91
	Av. Quan.	8	8	28	21	132	165	11	2
Hogs	% Resp.	17	67	17	50	0	100	100	100
	Av. Quan.	10	14	5	12	0	126	8	2
Cash Crop	% Resp.	20	100	40	0	0	80	80	80
	Av. Quan.	10	7	19	0	0	127	12	3
Cattle	% Resp.	0	100	25	50	25	100	100	100
	Av. Quan.	0	11	8	8	100	125	10	2
Poultry	% Resp.	0	100	100	0	100	100	100	100
	Av. Quan.	0	50	20	0	15	91	10	1
Total Surveyed Farm Operations	**% Resp.**	**11**	**78**	**26**	**30**	**22**	**96**	**96**	**93**
	Av. Quan.	**9**	**12**	**18**	**14**	**129**	**141**	**10**	**2**

TABLE 3 Current Waste Disposal Methods as Reported by Farm Operators.

Waste Type	Waste Disposal Practices: Burn %	Store %	Landfill %	Recycle %	Reuse %	Total
Pesticide	60	0	39	0	1	**100**
Fertilizer	98	0	0	0	2	**100**
Machinery						
i) Oils	15	5	0	0	80	**100**
ii) Oil Filters	8	0	92	0	0	**100**
iii) Batteries	0	37	4	59	0	**100**

Note: - Waste quantities were not collected for house, yard and other wastes.

Table 4 Pesticide Container Rinsing Practices as Reported by Those Who Apply Their Own Pesticides.

Farm Type	No. of Rinses Prior to Disposal				
	0	1	2	3or>	Until Clean
Dairy	1	2	2	2	1
Hogs	0	0	4	1	0
Cash Crop	0	0	1	2	0
Cattle	1	0	1	1	1
Poultry	0	0	1	0	0
TOTALS	**2**	**2**	**9**	**6**	**2**
% Population	**10**	**10**	**43**	**29**	**10**

Note: About 78% (21 of 27) of those surveyed reported applying their own pesticides.

TABLE 5 A Comparison of Percentage of Survey and Perth Co. Data as Related to Crop Type

Crop Type	% of Survey Growing Crop	% of Survey Acreage	% of Survey Pesticide Waste	% of Perth Growing Crop(1)	% of Perth Acreage(1)	1983 Ontario Pesticide Use (2)
Corn	90	38	78	86	31	43
Wheat/Grain	67	15	3	45	22	4
Soybeans	38	14	12	12	4	15
W. Beans	29	7	6	20	6	1
Barley	24	6	1	30	8	-
Hay	19	4	0	63	18	-
Alfalfa	10	6	0	-	0	-
Oats	10	1	0	5	1	-
Pasture	62	9	0	35	9	-

Note: 21 of 27 farms reporting
Perth County: corn=silage+grain corn; wheat/grain = mixed grains; hay=tame hay (from OMAF, 1987)
(1) from OMAF, 1987.
(2) from McGee, 1984

C18

MUNICIPAL SOLID WASTE FEASIBILITY OF GASIFICATION WITH PLASMA ARC

PHASE II - ENVIRONMENTAL ANALYSES

Presented to
The Ministry of the Environment
1989 Technology Transfer Conference
November 21, 1989

BY
A.V. Tsangaris
Resorption Canada Limited
2610 Del Zotto Avenue, RR#5
Gloucester, Ontario
K1G 3N3

BACKGROUND

Resorption Canada Limited (RCL) has been actively involved over the past few years in R&D with plasma arc technology, utilizing a specially designed 150KW plasma arc torch. Over the years a wealth of experience and knowledge has been gained in the plasma arc processing of carbonaceous materiels, pyroprocessing of ores and concentrates, and in industrial heat applications. A major area of concentration has been gasification, whether for the creation of a usable product gas, for the destruction of a waste materiel, or for a combination of both. A Plasma Heating System (PHS), when utilized in a reactor vessel with the exclusion of oxygen, can be used very efficiently for the gasification of any carbonaceous materiel. The resultant pyrolysis provides for virtual complete gasification of all combustibles in the source materiel, while non combustibles are reduced to a virtually inert slag. Municipal Solid Waste (MSW), with its high carbonaceous content, is such an application, which combines energy production with the destruction of a waste materiel with what has always been considered to be minimal environmental pollution. Plasma gasification of MSW is, therefore, considered to be a very substantial alternative to current forms of disposal.

The characteristics of plasma gasification of MSW were developed a number of years ago, however, prospective clients viewed the results as inconclusive since they were neither performed nor published in Canada, and there were no operational systems in either Canada or the US which utilized this technology in this application. In an effort to substantiate these operational characteristics and include an assessment of the environmental acceptability of the process, RCL, OBOE Engineering Limited and Ontario Hydro Research Division submitted an unsolicited proposal to the Ontario Ministry of Energy for funding support for a

feasibility study to investigate the plasma gasification of MSW. The proposal was divided into two Stages, Stage 1 to determine the overall process heat balance and the Higher Heating Value of the product gas, and Stage 2 to assess the environmental acceptability of the process as a whole including the combustion of the resultant product gas. Stage 1 was subsequently approved for a 1 April 1986 commencement and the approval of Stage 2 was to be reassessed on the basis of the results obtained through Stage 1.

Stage 1 was completed in February 1988 with 44 hours of experimental processing being performed. The final cost was $296,000, of which the Ontario Ministries of Energy and Environment cost shared 49.7%. Ontario Hydro provided both in-kind and cost sharing funding to a total of 22.8%, and the remainder was cost shared by RCL, OBOE Engineering and Plasma Energy Corporation of Raleigh, North Carolina. A summary of the results obtained and extrapolated to a commercial sized system compared to the results originally forcasted is as follows:

	Originally Forcasted	Commercial Size Extrapolated
Conversion Ratio	4.99:1	4.30:1
Overall Efficiency	80.6%	72.2%
Product Gas/Refuse HV Ratio	0.961	0.868
Product Gas HHV (BTU/SCF)	300-350	282.15 (max)
Dry Refuse/Slag Weight Reduction	-	5.37:1
Wet Refuse/Slag Weight Reduction	4:1	8.06:1
Refuse/Slag Volume Reduction	20:1	154:1
Power per Tonne Refuse (KWhrs)	550	612

Conversion ratio is defined as the energy available in the product gas compared to the electrical energy input to the process which created the product gas. A conversion ratio of 4.3:1 therefore means that for every BTU of thermal

energy input to the process through the plasma arc torch there are 4.3 BTUs of useable energy in the product gas. This ratio only considers the energy in the product gas, it does not consider any energy recovery of the sensible heat in the product gas which exits the reactor vessel virtually at the processing temperature. The energy balance derived through this experimentation is enclosed at Figure 1.

The product gas had the following chemical composition at the maximum heating value obtained through this experimentation:

Hydrogen	41.2%
Carbon Dioxide	8.3%
Ethylene	0.1%
Acetylene	0.2%
Oxygen	0.3%
Nitrogen	17.0%
Methane	3.2%
Carbon Monoxide	29.7%
Heating Value	282.2 BTU/SCF

The by-product slag obtained through this experimentation had the following chemical composition:

Carbon	0.71%
Silicon	12.60%
Calcium	1.67%
Iron	6.85%
Aluminum	3.54%
Sulphur	0.31%
Ash	77.30% (at 900 degC)

With these favourable results in hand, RCL and Ontario Hydro Research Division resubmitted Stage 2 to the Ministry of Energy for cost sharing consideration and, with approval, Stage 2 formally commenced on March 6, 1989. This project

will follow-on directly from the previous experimentation and investigate the environmental characteristics of the product gas, the products of combustion of the product gas and the by-product slag, as well as potential commercial applications of the by-product slag. The product gas will be analyzed directly from the gasification process and also after storage for an extended period of time. In addition, a leachate toxicity test will be performed on the slag. All environmental analyses will be performed by an independent analyses firm selected on the basis of cost and familiarity with the particular analyses. The estimated $237,000 cost of the project will be cost shared 45% by the Ministries of Energy and Environment, 13% by Ontario Hydro, and the remainder by RCL and a US developer from Cleveland, Ohio.

The environmental aspects of the process which will be investigated will include:

- analysis of the product gas, the condensate extracted from the drying of the product gas, and the products of combustion of the product gas for PCB, PAH, CB, CP, PCDD, PCDF, acid gases and trace metals; and
- analysis of the resultant slag for trace metals and leachate toxicity.

THE EXPERIMENTAL PROCEDURE

MSW throughput in the RCL plasma research facility, depicted at Figure 2, is estimated at 300-400 pounds per hour. Each experimental run covers a four to eight hour period, therefore, upwards of two tons of MSW are required per run. Either shredded or "as-received" city refuse can be accommodated, however, the use of shredded permits easier and more accurate ultimate and proximate analyses for comparison purposes. Steam can be introduced at varying rates, as required, to provide additional oxygen to react with the free carbon forming additional CO and H2.

The control system is very versatile and enables one operator to process varying amounts of materiel from next to nothing to the maximum capability of the facility depending on the type of materiel being processed. The operator has continuous readout of critical operational parameters of the process.

The process temperature, as monitored at the inside wall of the reactor vessel, is approximately 1100 deg C. Once the operating temperature is achieved, processing commences. MSW is weighed and then placed in the feed hopper for hydraulic feed into the vessel. The hydraulic system is adjustable to permit a variable rate of input materiel to be fed into the vessel. The pyrolysis operator monitors the processing rate through the temperature sensors in the vessel. An increasing temperature indicates that the vessel is emptying and a lowering temperature indicates that the MSW is being fed too rapidly. The optimum feed rate for the process is, therefore, achieved and maintained.

Output slag is permitted to accumulate in the bottom of the reactor vessel and is removed through a trap door by hydraulically tipping the entire vessel. At a 20 to 1 volume reduction ratio between the input materiel and the output slag a full experimental run can be conducted without the need for slag output. The slag is poured into a bed of silica sand.

The volume of product gas generated is continuously recorded on a Bailey gas meter, which is calibrated prior to the commencement of any experimentation, and a continuous log of all torch operating parameters are maintained to facilitate full analyses at a later time. The product gas chemical composition is monitored on a periodic basis with a Gas Chromatograph to ensure a good cross sectional reading

of the product gas quality. The product gas can be combusted in a burner directly from the gasification process, or it can be compressed and stored for future combustion. Excess product gas is flared on exit.

Environmental analyses will be conducted in accordance with the MSW gasification process flow diagram at Figure 3.

CURRENT STUDY STATUS

Activity to-date through the project concentrated on discussions with the Environmental Analyses firms to establish the desired procedure, scope and costing of the environmental analyses, and preparing the plasma research facility for the experimentation. Some delay was experienced due to changing conditions for the environmental analyses. The major changes to the facility entailed the addition of the capability to store the product gas for later use. Full results from the study should be available shortly.

BENEFITS/ADVANTAGES

The success of this study to prove the environmental acceptability of the process, in conjunction with the operational characteristics of the plasma gasification of MSW previously developed through Stage 1, could be extremely beneficial for this application, coming at a time when new and more environmentally acceptable solutions are sorely needed. This would not only open up a complete new application field for this emerging technology but it could be a significant boon to an ever increasing number of municipalities with existing city refuse problems. This would not merely be another way to get rid of MSW, but it could be a technological breakthrough with significant benefits. The major benefits from this process could be:

- the standard output product of the plasma arc process is a producer gas which offers considerably more

flexibility for use than, for example, sites which only produce steam;

- plasma arc gasifiers can have substantially lower capital costs since they can integrate more fully into a potential owner's existing facility, as compared to sites which require integral steam boilers thereby increasing the cost of these sites by 25 to 30%;
- the output energy of the plasma arc gasifier, being a producer gas, can be stored for future use similar to natural gas, as compared to steam boiler installations where the energy is lost if it is not used virtually immediately;
- the operating temperature and the heat transfer rate of the plasma arc process can be variable, at will, therefore, the optimum operating temperature and rate of reaction can be achieved, varied and maintained to minimize undesirable output pollution products and maximize the energy recovered from the input materiel;
- the plasma arc gasification process does not depend on the combustion of any of the input materiel for the pyrolysis process, therefore, the quantity of output energy produced per unit of input materiel can be maximized;
- plasma torches have the potential to deliver the heat of reaction much faster than conventional heat sources enabling the complete breakdown of the input materiel and the production of smaller molecules which are inherently less hazardous;
- the ability to process materiel at any rate from next to nothing up to the maximum capacity and still operate at the optimal operating point is a very desirable feature;
- the fact that the materiel enters into two chemical reactions, once during the pyrolysis process and once during the combustion process, before being exhausted

to the atmosphere ensures minimization of pollutants;
- metallics and glass in the input materiel melt, thus substantially reducing the volume of the output slag and alleviating problems with its disposal; and
- there is a potential commercial market for the slag produced through plasma arc gasification of MSW thereby virtually eliminating the requirement for continued operation of controlled land fill sites for MSW.

DISADVANTAGE

The primary disadvantage in this process is the operating costs associated with the high electrical consumption. This cost is somewhat offset by the higher volume of product gas generated and, in some cases it can be further alleviated by operation at lower power during peak hydro usage periods. For example, demand charges can be 30%-90% lower, depending on the hydro district, for operation between 8PM and 8AM and all day Saturday and Sunday, which potentially can be used to advantage. Cogeneration could also be very advantageous to offset the hydro operating costs. Initial assessment of cogeneration indicates that the full process could be virtually self sustaining.

CONCLUSION

The participants in this feasibility study remain very optimistic that the experimentation will be highly successful and the plasma gasification of Municipal Solid Waste will become a fact of the future.

ENCLOSURES

FIGURE 1 - COMMERCIAL SYSTEM HEAT BALANCE
FIGURE 2 - PLASMA RESEARCH FACILITY
FIGURE 3 - PLASMA GASIFICATION PROCESS WITH ENVIRON ANALYSES

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MUNICIPAL SOLID WASTE YIELDS

FIGURE 1 - COMMERCIAL SYSTEM HEAT BALANCE
(FROM R&D RESULTS FEBRUARY 1988)

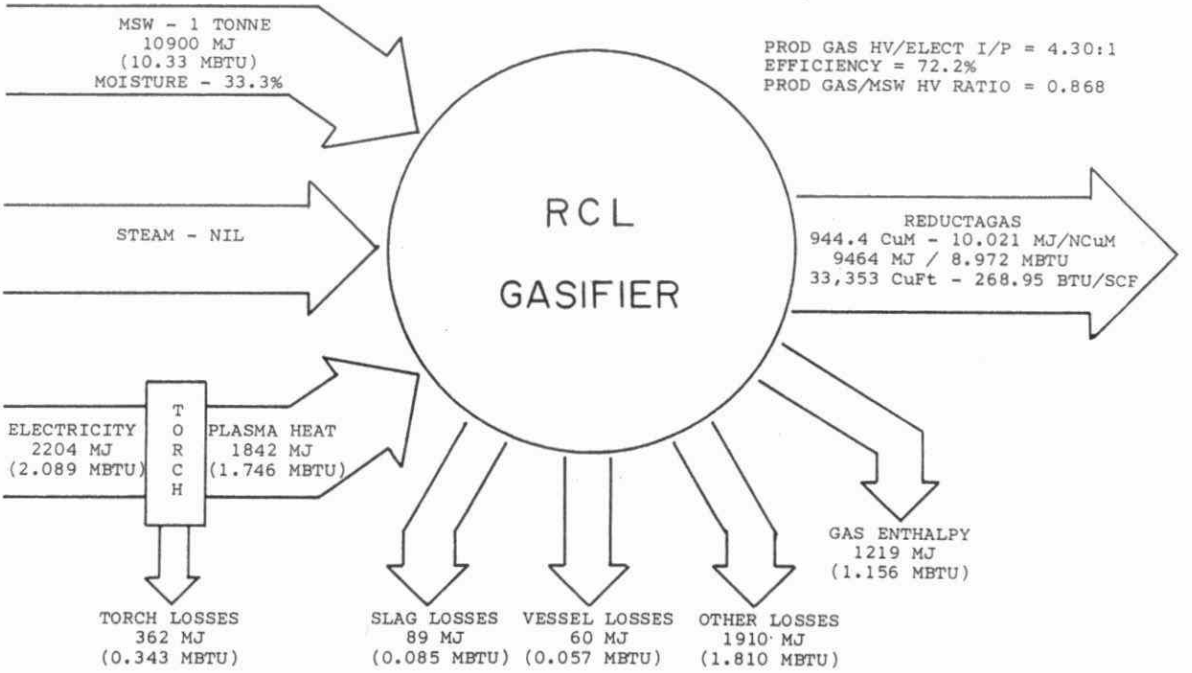

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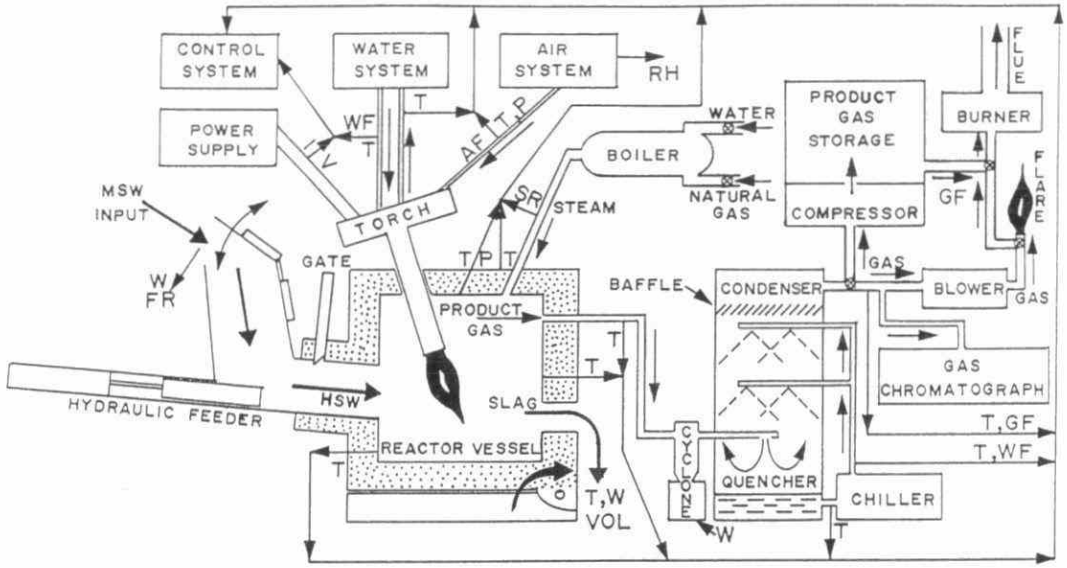
FIGURE 2 - PLASMA RESEARCH FACILITY



I—CURRENT (AMPS) V—VOLTAGE (VOLTS) T—TEMPERATURE (DEGREES C) GF—GAS FLOW (SCFM)

P—PRESSURE (PSIG) W—WEIGHT (LBS) RH—RELATIVE HUMIDITY (%) WF—WATER FLOW (GPM)

FR—FEED RATE (LBS/HR) SR—STEAM RATE (LBS/HR) AF—AIR FLOW (CFM) VOL—VOLUME (CF)

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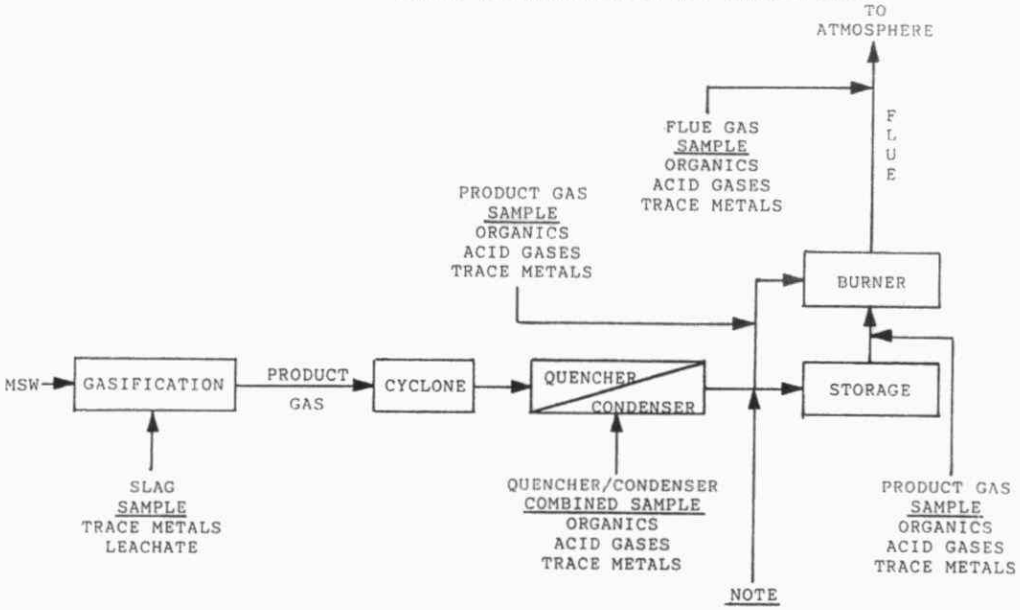
FIGURE 3 - PLASMA GASIFICATION PROCESS
WITH ENVIRONMENTAL ANALYSES



NOTE: Product gas can be either stored at this point or routed directly to the burner for combustion depending on the analyses required.

VOLUME II

SESSION C

LIQUID & SOLID WASTE RESEARCH

POSTER PRESENTATIONS

DEVELOPMENT OF BACKFILL AND CONSTRUCTION APPLICATION GUIDELINES FOR ONTARIO.

Maria Kelleher* and B. Whiffin
CH2M HILL ENGINEERING LTD.
Mississauga, Ontario, L5N 1V9

Tentative guidelines were developed for the classification of industrial waste and by-product materials for backfill and construction applications. The effectiveness and reliability of these tentative guidelines were tested through a field program which examined the impact of blast furnace slag, fly ash and foundry sands on groundwater downstream of sites which contained relatively large volumes of each of these materials. The program involved a hydrogeological investigation of each site, bulk chemical characterization of the material placed at the site, and acetic acid and distilled water leachate extraction procedures carried out on the material placed at each site. Groundwater both upstream and downstream of the site was analyzed. The purpose of the field study was to assess the extent to which results of the bulk chemical characterization and leachate tests are an indication of the impact of material placement on downstream groundwater quality. Bulk chemical characterization procedure results were compared to acceptable soil concentrations in Ontario, and values provided in the Decommissioning Guidelines and also in the Draft Dredgate and Lakefill Guidelines. The acetic acid and distilled water leachate results were compared to leachate values presented in Draft Dredgate and Lakefill Guidelines and also in Regulation 309 and interim MOE guidelines for inert material. Groundwater quality values were compared to Ontario, U.S. and WHO surface water and drinking water quality objectives and also to the groundwater reasonable use policy.

CP2 "INTEGRATED WASTE MANAGEMENT PLANNING IN ONTARIO - PROGRAM, PROCESS, AND PERSPECTIVES"

BY

Susan Clarke, P. Eng., Beverley Alder,
Hans Mooij, P. Eng.
Waste Management Policy Section
Waste Management Branch
Ontario Ministry of the Environment
Toronto, Ontario.

In Ontario, any municipality with a landfill serving a population greater than 1,500 has to undertake an Environmental Assessment Study before it can expand the site or operate a new waste disposal facility. Legislation mandates that such a Study assess the net environmental effects of alternatives to waste disposal, as well as alternative means of waste disposal, to ensure that the best environmental waste management options are evaluated in terms of the needs and opportunities for the communities being served.

Recognizing the need to assist municipal governments in undertaking environmental impact assessments and proper waste management planning, the Ontario Ministry of the Environment initiated a Waste Management Master Plan funding program in 1982. This introduced a formal, integrated and long-term planning approach to area waste management studies.

Master Planning Studies, undertaken regionally or by groups of municipalities, are designed to develop comprehensive waste management plans through a staged evaluation of alternatives, based on a hierarchy of waste management options. Of primary importance is the need to reduce the volumes of waste requiring final disposal by integrating 3R's systems and solutions. Alternatives are evaluated based on technical merit as well as the effects on the environment, which is broadly defined to include the social, cultural, and economic as well as natural environment.

The Master Plan Studies identify and evaluate needs and opportunities for the grouped municipalities in terms of identifying reasonable system components, system options, and selection of facility sites, as well as identifying markets for recycled materials. Full public involvement in planning and decision-making is required. Completed Plans detail the selected system and sites, and present a blueprint for implementation administration and financial management of the Plan. Formal approval is sought for all or part of the preferred system, in accordance with a provincial approvals process which may include a full public hearing.

CP3

CHARACTERIZATION OF THE FECAL INDICATOR BACTERIAL FLORA OF SANITARY SEWAGE WITH APPLICATION TO IDENTIFYING THE PRESENCE OF SANITARY WASTE IN STORM SEWERS

P.L. Seyfried*, E. Bauer, I Huh, S. Shibata,
E. Hani, R. Harmandayan and T. Bleier

Department of Microbiology, FitzGerald Building
University of Toronto, Toronto, Ontario
M5S 1A8

Storm sewers are designed to channel untreated storm water into surface waters. An unusually high dry weather flow of storm sewage along with high fecal coliform counts indicate that there may be potentially hazardous sanitary connections in the storm sewer line. The objective of this study was to assess the use of bacterial indicators to trace illegal sanitary connections to storm sewers. The indicators selected for study were Escherichia coli, fecal coliforms, fecal streptococci, enterococci, Pseudomonas aeruginosa, Clostridium perfringens, and Bifidobacterium sp. The organisms were collected from specific sites in sanitary sewer lines, and from priority and nonpriority storm sewers during periods of wet and dry weather as well as from surface water runoff. The bacterial isolates were subjected to biochemical testing, serotyping and genotyping. The results showed that Streptococcus casseliflavus was primarily recovered from surface runoff and nonpriority storm sewers. On the other hand, higher concentrations of bifidobacteria were isolated from sanitary and high priority storm sewage than from nonpriority storm water. These data suggest that a ratio of Bifidobacterium to S. casseliflavus counts may be used to trace the location of human and/or animal fecal wastes. Additional field studies are needed to confirm the applicability of these ratios.

INTRODUCTION

The Toronto Area Watershed Management Study was initiated in 1981 to better define the water quality at Toronto Beaches and in the Black Creek, Humber and Don Rivers. Particular emphasis was placed on urban areas of Metropolitan Toronto, especially on point pollution inputs, because of the high levels of fecal indicator bacteria that were found in storm sewages. Subsequent studies were initiated in the fall of 1982 to assess the contribution of pollution loading by the storm sewers and to trace the source of pollution in the storm sewer lines.

The Ministry of the Environment designated storm sewer outfalls discharging more than 1 L/sec. during dry weather periods and exhibiting fecal coliform densities of greater than 10,000 FC/100 mL as high priority. Efforts were made to identify and eliminate the source of the fecal pollution in these sewage lines but pinpointing the original source of pollution was difficult because specific bacterial indicators of human fecal waste were not available. To reduce fecal contamination in storm sewers detection methods that can locate fecal inputs and differentiate between human and nonhuman sources of pollution are required.

Traditionally, Escherichia coli and fecal coliforms have been used as the indicators of fecal pollution in storm waters and surface waters but, due to their wide distribution in both human and animal feces, they are not acceptable as an indicator of strictly human input.

Mossel (1958) was the first to propose bifidobacteria as potential indicators of fecal contamination. More recently, a number of authors (Buchanan and Gibbons, 1974; Levin, 1977; Cabelli, 1979; Resnick and Levin, 1981) have suggested that bifidobacteria could be used to distinguish between human and animal fecal pollution. However, the usefulness of bifidobacteria as

a specific indicator of human fecal pollution may be limited due to the short survival of the organism in the extra-intestinal environment (Resnick and Levin, 1981; Oragui, 1982). Before bifidobacteria can be used as an indicator of recent human fecal contamination in the Toronto area, their survival in the environment and their ability to satisfy the parameters of a good indicator must be investigated.

The purpose of this study was to characterize the bacterial populations found in urban storm and sanitary wastes in an attempt to develop a methodology for the detection of human fecal wastes in storm sewer lines. The information presented in this report constitutes additional data not published in the 1987 or 1988 Technology Transfer Conference Proceedings (Seyfried et al. 1987; Seyfried et al. 1988).

METHODS

Sampling Sites

Table 1 and Figure 1 indicate the sites surveyed in the Mount Steven Trunk storm sewer line. Locations A, B and C were sampled because this area was designated a high priority sewer by the Ministry of the Environment. The nonpriority sites, selected for comparison, were X, Y and Z in the Mount Steven Trunk storm sewer branch lines. During periods of wet weather, storm water run-off was also collected at the X, Y and Z sites. These samples were labelled R, G and Q, respectively. Samples D, E and F were obtained from a sanitary sewer in close proximity to the priority storm sewer sampling points.

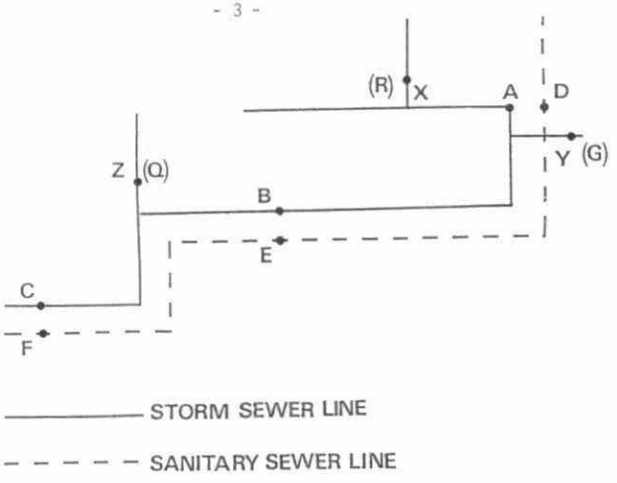


FIG. 1 - Schematic diagram of Mount Steven storm sewer and sanitary sewer lines.

TABLE 1. Sampling locations of high priority and non-priority storm sewers, sanitary sewer and storm water runoff.

Sample Description	Code	Site
High Priority Storm Sewer Line, Mount Steven Storm Sewer Trunk	A	Danforth and Jones Avenues - furthest in-line sampling point (near source of suspected solution input)
	B	Pape and Strathcona Avenues (mid-line sampling point).
	C	First and Broadview Avenues (near outfall).
Non-Priority Storm Sewer Branch Lines	Y	Chatham and Jones Avenues (connects to main line above sampling point B).
	X	Danforth And Woodycrest Avenues (connects to main line above sampling point A).
	Z	Pape and Cavell Avenues.
Storm Water Runoff	G	Chatham and Jones
	R	Danforth and Woodycrest Avenues
	Q	Pape and Cavell Avenues
Sanitary Sewage Line	D	Danforth and Jones Avenues
	E	Strathcona and Pape Avenues
	F	First and Broadview Avenues

Sample Collection

During periods of dry weather, triplicate samples were collected from each sampling point in the sewers over a four-day period. The dry weather samples were obtained in October, 1986; June, 1987; August, 1987; June, 1988; and August, 1988. Wet weather samples were collected from the sewers and the street run-off during rainy days in July, September and October, 1987.

The samples were collected in sterile glass containers, transported to the laboratory on ice, and processed within 6 hours of collection.

Fecal specimens from both humans and animals were also obtained.

Bacterial Isolation and Enumeration

Analysis of the samples for indicator bacteria was by membrane filtration of appropriate dilutions of the samples through Gelman GN6 47 mm cellulose nitrate filters with a pore size of 0.45 um (Standard Methods, 1985). The filters were planted on media appropriate for the recovery of the various indicator bacteria.

Fecal coliform bacterial densities were determined by planting the filters on m-TEC agar (Dufour *et al*. 1981) and incubating for 23 $\pm$ 1 hours at 44.5 $\pm$ 0.5° C. Both target and non-target colonies were counted. Target colonies were yellow, yellow-green and yellow-brown; non-target colonies were blue to blue-green in colour. To ensure the accuracy of the counts, only results obtained from filters with target counts of between 10 and 100 colonies were used to calculate the bacterial density per 100 mL of water sample.

A second step for the determination of *E. coli* by urease treatment (Dufour and Cabelli, 1975) was incorporated into the m-TEC procedure. Filters with appropriate target counts (i.e. between 10 and 100 target colonies) were

removed from the m-TEC plates and placed on filter pads soaked in a urea phenol red solution (Dufour and Cabelli, 1975). The filters remained in contact with the filter pad for 15 min to allow for deaminization by non-E. coli coliform bacteria processing urease. A second count of all urease negative colonies (all yellow, yellow-green and yellow-brown colonies) was taken.

Fecal streptococci determinations were made by planting the filters on m-Enterococcus agar (Difco) (APHA, 1985). The medium was incubated for 48 hr at 35° C and a count of all pink to purple target colonies taken. Upper and lower counting limits of 10 to 150 target organisms were applied to the reported results.

Enterococci were recovered on m-ME agar (APHA, 1985) which also contains indoxyl-B-D-glucoside (IG). The m-ME plates were incubated for 48 hr at 41.5 ± 0.5° C. The incubation time was modified from the original 24 hr suggested by Dufour as it allowed for a slight increase in recovery of target organisms. The addition of IG to the medium facilitates differentiation of the B-D-glucosidase enterococci from other fecal streptococci. Both target and non-target colonies were enumerated. Target colonies on m-ME were purple, white-blue to dark blue with blue haloes from degradation of the IG. Non-targets were pink to maroon non-haloed colonies. Counting range limits of 10 and 150 were also applied to these results.

Pseudomonas aeruginosa densities were determined using m-PA agar (APHA, 1985). The medium was incubated at 41.5 ± 0.5° C for 48 hr and a count of all flat spreading brownish-green or tan colonies obtained. Upper and lower counting limits of 10 and 150 were applied to the results.

Bifidobacterium spp. were isolated on the YN-17 medium described by Mara and Oragui (1983). Target bifidobacteria colonies appear dark blue to black.

Greenish coloured colonies were not counted; however, to ensure that all bifidobacteria were enumerated, crystal violet stains were made of colonies that had a different size or colour. Adjustments to the counts were made if necessary.

Three other media, MPN (Tanaka and Mutai, 1980), MRS (Oxoid), and HBSA (Mara and Oragui, 1983) were used for comparative recovery studies.

Clostridium perfringens was isolated using a medium originally developed by Bisson and Cabelli (1979) and modified by the Ministry of the Environment Southeastern Region Laboratory (m-CP2) (M.O.E., 1986). The samples were pretreated at 70° C for 15 or 30 min to destroy the vegetative cells. Appropriate volumes of the samples were passed through membrane filters and the filters were placed on m-CP2 plates. The plates were then incubated anaerobically at 37° C for 48 hr. Target colonies appear yellow with a large black centre which can extend fairly close to the circumference; the colonies do not possess a blue halo. Non-target colonies have a blue halo and they can be yellow or yellow with a black centre.

Bifidobacteria and E. coli Survival Studies

The 50 mL dialysis membrane diffusion chambers used in the study were designed by McFeters and Stuart (1972). The 48 hr broth cultures of E. coli, B. breve, and B. bifidum as well as the fecal and sewage isolates of bifidobacteria were centrifuged and washed three times in gelatin phosphate buffer. Following resuspension and dilution, the bacteria were suspended in sterile L. Ontario water and added to the chambers. The chambers were then immersed in a glass tank containing L. Ontario water at room temperature. Disposable 10 mL luer-lock syringes were used to collect the bacterial samples

at 2, 5, 12, 24 48 and 72 hr. Bacterial densities were enumerated by appropriately diluting, membrane filtering and planting the filters on YN-17 and m-TEC media. All samples were analyzed in triplicate.

RESULTS AND DISCUSSION

Enumeration of Fecal Indicator Bacteria in Sewers

The comparative levels of fecal coliforms (FC), Escherichia coli (EC), fecal streptococci (FS) and Pseudomonas aeruginosa in storm and sanitary sewage during dry weather are shown in Figs. 2 and 3. The three sites (A, B and C) in the high priority storm sewer had FC geometric mean concentrations ranging from 10^3 to 10^4 with an EC range of 10^2 to 10^3. It should be noted that FC and EC concentrations of this magnitude are suspiciously high for storm water and suggest an input of sanitary waste contamination. The densities of FS were in a slightly lower range and P. aeruginosa levels were low in comparison with the other bacterial indicators.

As would be expected, the FC, EC and FS concentrations in sanitary sewage were approximately an order of magnitude higher than the levels observed in storm sewers. The P. aeruginosa count was observed to be around 10^4 per 100 mL in the sanitary sewers; this was considerably higher than the 10^1 counts observed in storm sewers.

During a dry weather survey the following year (Figs. 4 and 5), comparable results were obtained for FC and EC densities. As may be seen in Fig. 4 the observed counts were higher at points A and B, the suspected site of contamination in the storm sewer. Analysis of Bifidobacterium and Clostridium perfringens levels in storm and sanitary sewage produced interesting results. As was observed for the FC and EC determinations the bifidobacteria counts were

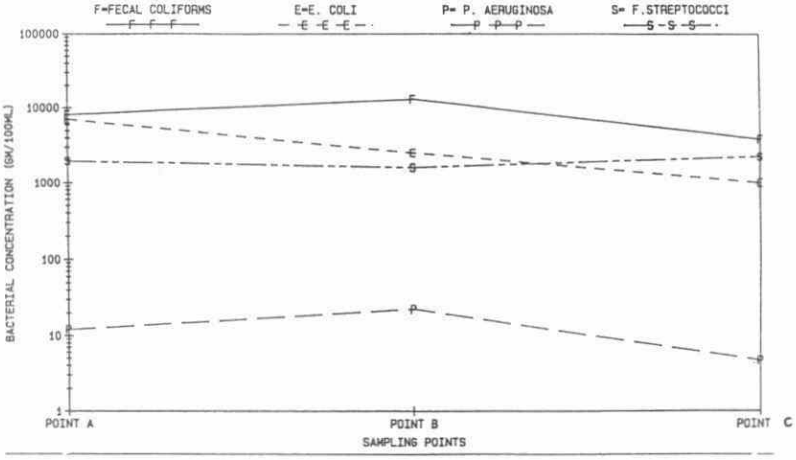


Fig. 2 Geometric mean concentrations of fecal coliforms, E. coli, P. aeruginosa and fecal streptococci in storm sewage sampled during October and November, 1986

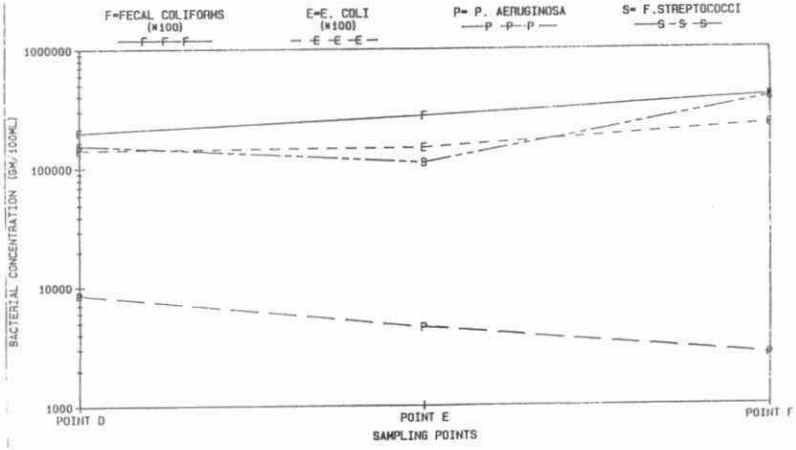


Fig. 3 Geometric mean concentrations of fecal coliforms, E. coli, P. aeruginosa and fecal streptococci in sanitary sewage sampled in October and November, 1986

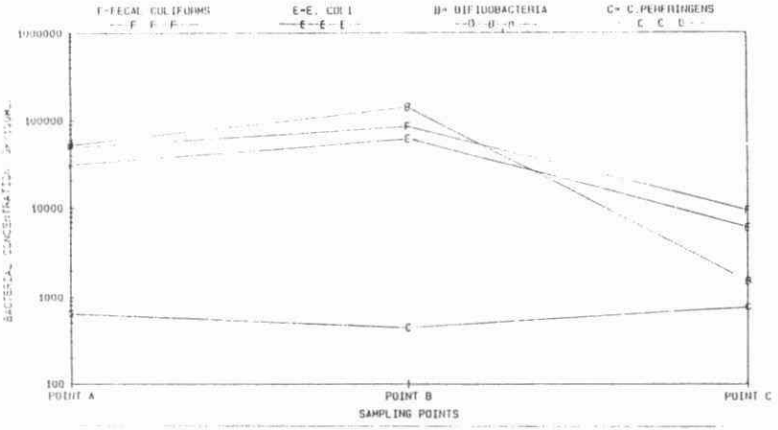


Fig. 4 Geometric mean concentrations of fecal coliforms, E. coli, Bifidobacterium spp. and Clostridium perfringens in storm sewage during the June 1987 dry weather survey

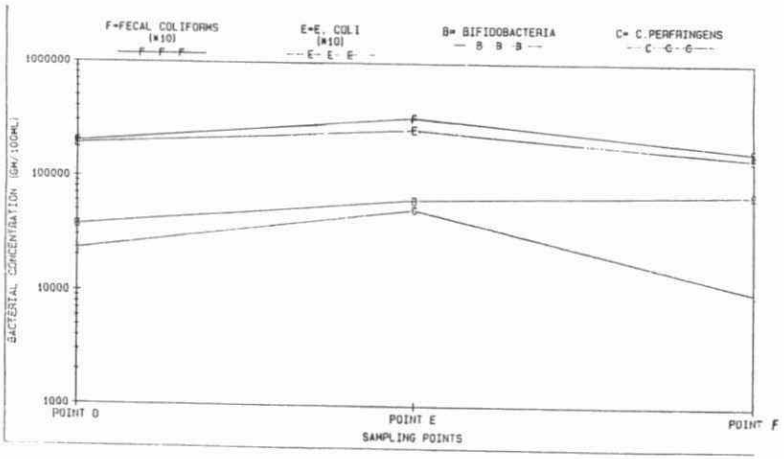


Fig. 5 Geometric mean concentrations of fecal coliforms, E. coli, Bifidobacterium spp., and Clostridium perfringens in sanitary sewage during the June 1987 dry weather survey

highest at sites A and B in the storm sewer and dropped off at point C. Clostridium perfringens levels, on the other hand, increased rather than decrease at point C. This might be expected since, rather than dying off, C. perfringens spores have a tendency to build up and accumulate in the system. Because C. perfringens is present in high densities in human and animal feces levels in the sanitary sewage were in the 10^4 range compared with 10^2 densities in storm sewage.

The aforementioned enumeration results show that levels of all the bacterial indicators demonstrate that there is fecal input in the storm sewer line. Bifidobacteria and P. aeruginosa appear to have potential as indicators of a human source of contamination. Because C. perfringens produces spores that remain in the system, this organism is not effective as a point-of-impact indicator.

Selective Media for the Recovery of Bifidobacteria

Four media, MPN, MRS, YN-17 and HBSA, were used to recover bifidobacteria from sewage and fecal samples. The results showed that the MRS medium was often highly contaminated with streptococci and lactobacilli. YN-17 and MPN, on the other hand, were equally selective for bifidobacteria with less than 3% contamination by fecal streptococci. However, MPN required an incubation time of 48 hr before visible growth occurred, whereas the incubation time required for YN-17 was 24 hr.

There were discrepancies between the findings of this study and those of Mara and Oragui (1983) with respect to the YN-17 medium. Mara and Oragui found flat, non-mucoid colonies measuring 2 to 4 mm and dark green in colour to be background streptococci. They distinguished domed, mucoid colonies measuring 1

to 2 mm and pale green with a pale green periphery as being bifidobacteria. This study showed the opposite to be true. The smaller, dark green or blue flatter colonies were identified as bifidobacteria and those exhibiting a pale green periphery were contaminating streptococci or a mixture of bifidobacteria and streptococci. Any colonies pale green in colour that did not contain a darker centre were found to be streptococci.

The HBSA medium could be used to isolate sorbitol-fermenting species of bifidobacteria but, once again, there was a problem with contaminating streptococci. In comparison, the YN-17 medium yielded higher concentrations of the organism and isolated a broader spectrum of different species of bifidobacteria than did HBSA.

Bifidobacteria were isolated from fecal specimens in concentrations 10 to 100 times greater than E. coli. However, in sewage samples the counts of Bifidobacterium were lower than those of E. coli. This could be due to a dilution effect and also to the fact that species of Bifidobacterium tend to die off at a faster rate in the environment (Oragui, 1982).

Speciation of Bifidobacteria

When the Bifidobacterium isolates were speciated it was found that a wider variety of bifidobacteria species were recovered from sewage samples than from fecal samples (Fig. 6). The predominant species in human feces and sewage were the sorbitol-fermenting B. adolescentis and B. breve. As indicated in Fig. 6 B. breve was isolated from cat fecal samples but none of the cat isolates were found to be sorbitol-fermenting. Mara and Oragui (1983) have proposed that sorbitol-fermenting bifidobacteria be used as indicators of human fecal pollution. Because, as cited earlier (Seyfried et al. 1988), we have been able

to isolate B. adolescentis from dogs and B. breve from chicken feces this approach should be viewed with caution.

Bifidobacterium Survival

The advantages of using bifidobacteria as fecal indicator bacteria are that they exist in high numbers in both feces and fecally contaminated environments. Furthermore, they supposedly do not multiply outside the body. The limitations associated with the use of bifidobacteria as a specific indicator of human fecal pollution relate to the organism's short survival time outside the intestine (Resnick and Levin, 1981; Oragui, 1982). Previous survival studies have shown bifidobacteria to die off more rapidly than E. coli upon exposure to environmental waters (Carillo, Estrada and Hazen, 1985). Because too rapid a decline of bifidobacteria in the aquatic environment and subsequent indetectability could make the organism a poor indicator of fecal contamination this study compared the in vitro survival characteristics of bifidobacteria and E. coli using the dialysis membrane filter chambers devised by McFeters and Stuart (1972). Pure cultures of B. breve and B. bifidum as well as fecal and sewage isolates of bifidobacteria were studied. The comparative survival rates of B. breve and E. coli in Lake Ontario water at temperatures of 21 to 23° C are depicted in Fig. 7. In all cases the bifidobacteria cultures appeared to parallel the die-off trends in E. coli during the initial five hour period; thereafter, bifidobacteria began to show a slightly more rapid decline. The Bifidobacterium isolates died off within 24 hr of exposure to L. Ontario water whereas E. coli persisted for 48 hr. Dilution of nutrients and exposure of the pure culture to any toxic chemicals present in the water may have had an impact on the survival of the organisms.

The more rapid decline of the anaerobic bifidobacteria in comparison with the aerobic E. coli may be accounted for by oxygen diffusion into the chamber. The propensity of the bifidobacteria to be present in feces and to die off rapidly in the environment make them good indicators of recent fecal pollution.

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VOLUME II

SESSION D

ANALYTICAL METHODS RESEARCH

VERBAL PRESENTATIONS

D2

EVALUATION OF INDOXYL-B-D-GLUCURONIDE AS A CHROMOGENIC REAGENT FOR THE SPECIFIC DETECTION AND ENUMERATION OF ESCHERICHIA COLI IN ENVIRONMENTAL SAMPLES. A.N. Ley*, D. Fredenburgh, N. Rickey, K. Stovel, and M. Taylor, Ontario Ministry of the Environment, 133 Dalton Ave., Kingston, Ontario, K7L 4X6, and R.J. Bowers and S. Wolfe, Department of Chemistry, Queen's University, Kingston, Ontario, K7L 3N6.

The safety of water for drinking and recreational use is determined by testing for indicator organisms known as total and fecal coliform bacteria (Anonymous 1985). The traditional objective has not been to search for specific pathogens (a time-consuming, unreliable and costly procedure), but to test for the presence of harmless fecal bacteria that are always associated with enteric pathogens such as Salmonella and Clostridium species. Total and fecal coliforms are easily detected and quantified in water (Geldreich 1978).

The total coliforms are a closely related group of bacteria that include species belonging to Escherichia, Klebsiella, Enterobacter, Citrobacter, Serratia and Hafnia. With the exception of Escherichia coli, the total coliform bacteria are commonly associated with soil, vegetation, pulp wastes and sediments and are rarely found in high numbers in feces. E.coli, on the other hand, occurs as a natural inhabitant in the intestines of humans and animals and is seldom found in pristine environments (Dufour 1977).

Because of the diverse origin of total coliforms the fecal coliform test was developed to more readily identify E.coli as an indicator of sewage and fecal pollution. In addition to detecting E.coli, however, the fecal coliform procedure recovers Klebsiella, Enterobacter and Citrobacter as fecal coliforms.

Recently, a considerable amount of attention has been focused on developing rapid tests that are specific for the identification of E.coli. Kilian and Bulow (1976, 1979) showed that para-nitrophenyl-B-D-glucuronide, a chromogenic substrate for the enzyme, B-glucuronidase, provided a simple and rapid method for the detection of E.coli. Similarly, Feng and Hartman (1982), demonstrated that 4-methyl-umbelliferyl-B-D-glucuronide, a fluorogenic, glucuronidase substrate, provided a rapid, one-step method for the detection and enumeration of E.coli.

These procedures, however, have a number of limitations. Para-nitrophenyl and 4-methylumbelliferone are released by enzymatic hydrolysis from the corresponding glucuronides as reaction products. The diffusion of para-nitrophenyl prevents the identification of discrete bacterial colonies (Kilian et al. 1979, Ley et al. 1988). The detection of 4-methylumbelliferone by

fluorescent light is subject to interference on membrane filters (Farber 1986).

This presentation reviews the recent studies and current work on the use of the novel chromogenic chemical, indoxyl-B-D-glucuronide (IBDG), as a selective reagent for the specific detection and enumeration of E.coli in environmental samples. IBDG was evaluated as a reagent for the detection of E.coli by membrane filtration in environmental samples by Ley et al. (1988). The assessment of IBDG as a substrate for the rapid detection of E.coli in urine was reported recently by Delisle et al. (1989).

Slide 1.

The structure of indoxyl-B-D-glucuronide (IBDG) consists of an indoxyl aglycone moiety, attached in the B configuration to the C-1 anomeric carbon of glucuronic acid. Enzymatic hydrolysis of IBDG by E.coli B-glucuronidase liberates indoxyl and glucuronic acid. In the presence of oxygen (air), indoxyl rapidly oxidizes and combines to form water-insoluble indigo.

This is the first time that IBDG has been synthesized. The total synthesis of the molecule has been accomplished by Dr. Ray Bowers and Professor Saul Wolfe, Department of Chemistry, Queen's University, Kingston, Ontario.

Slide 2.

The analysis of raw sewage was compared by membrane filtration using a standard fecal coliform test (mTEC medium) and mTEC-IBDG agar medium (Ley et al. 1988). Dilutions of 10^{-3} and 10^{-2} ml of sewage were filtered through 0.45 micron membrane filters and the filters incubated on mTEC and mTEC-IBDG media, at 45 °C for 20 h. Fecal coliforms produced yellow-brown colonies on mTEC medium and E.coli developed as blue colonies on mTEC-IBDG medium. API 20E test strips [Analytab Products] were used to identify the isolates examined.

Slide 3.

This slide shows the growth of E.coli at 45 °C on EC agar medium supplemented with IBDG (0.8 g/L). The organisms were isolated directly from raw sewage.

Slide 4.

IBDG can be used to recover E.coli at 35 °C, the temperature used for the total coliform test. Blue colonies are easily counted in the presence of non-target background growth on EC-IBDG medium.

Slide 5.

E.coli streaked directly on the surface of EC-IBDG medium and incubated at 35 °C grow as well defined dark blue colonies.

Slide 6.
The colony growth of E.coli at 35 °C on lauryl sulphate agar supplemented with IBDG (0.8 g/L) is markedly more diffuse compared to growth observed on EC-IBDG medium.

Slide 7.
MacConkey agar supplemented with IBDG (0.8 g/L), provides a medium for the rapid differentiation of E.coli from other lactose positive, B-glucuronidase negative members of the Enterobacteriaceae family (Delisle et al. 1989). Glucuronidase positive E.coli developed as dark blue colonies after 18 h at 35 °C on MacConkey-IBDG agar. Enterobacter aerogenes and Enterobacter cloacae grow as dark red colonies on this medium.

The results of the direct screening of Lake Ontario and stormwater samples with mTEC-IBDG (0.8 g/L, sodium salt) are shown in Table 1. Representative blue and colourless colonies were isolated from individual membrane filters. The bacteria examined were recovered from approximately 10% of the 1600 samples collected. From a total of 206 gram negative isolates, there were 96 true positives, identified correctly as E.coli. Five false negatives, colourless E.coli colonies were detected. These results indicate a sensitivity of 95%. Out of a total of 105 negatives, 98 were true negatives (non-E.coli), and seven were false positives (blue colonies), giving a specificity of 93.3%.

The results of this study with mTEC-IBDG, indicate that this medium has a sensitivity and specificity of 95.0% and 93.3%, respectively, for Escherichia coli isolated from Lake Ontario and stormwater samples.

TABLE 1. B-glucuronidase activity on mTEC-IBDG agar medium

Organism	No. tested (n = 206)	No. IBDG positive*
Escherichia coli	101	96
Citrobacter freundii	5	3
Klebsiella pneumoniae	38	0
Klebsiella oxytoca	5	0
Enterobacter cloacae	28	0
Enterobacter agglomerans	1	0
Enterobacter sakazakii	5	0
Plesiomonas shigelloides	9	0
Serratia spp.	5	0
Hafnia spp.	2	1
Kluyvera spp.	2	2
Acinetobacter calcoaceticus	4	0
Flavobacterium sp.	1	1

*Blue colonies were recorded as positive.

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D3

PREPARATION OF FLUORANTHENO[1,2-b]THIOPHENE AND FLUORANTHENO[3,2-b]THIOPHENE FOR REFERENCE STANDARDS IN ENVIRONMENTAL ANALYSIS

I. [illegible] RUFF AND Y.S. CHUNG*

DEPARTMENT OF CHEMISTRY, YORK UNIVERSITY

4700 KEELE STREET, NORTH YORK, ONTARIO M3J 1P3

Under reducing conditions during the combustion of petroleum, coal and other fuels polycyclic aromatic hydrocarbons (PAH) are among the principal byproducts. Under the same conditions fuel-bound sulfur becomes incorporated into stable thiophene condensed aromatic derivatives. Sulfur isosteres of carcinogenic PAH's have been shown to exhibit levels of mutagenic activity comparable with their PAH isosteres.

Cyclopentene fused PAH's such as cyclopenta[c,d]pyrene have been found to be common environmental contaminants and show levels of mutagenic and carcinogenic activity that are comparable with those of benzo[a]pyrene.

In contrast to the carbocyclic systems relatively little is known about the biological properties of sulfur heterocyclic analogs of mutagenic and carcinogenic PAH's primarily due to the lack of standards. We have developed a method involving cyclobutanones as the key intermediate for the synthesis of novel cyclopentene-fused polycyclic aromatic thiophenes. The synthetic details of Fluoranthено[1,2-bithiophene and Fluoranthено[3,2-bithiophene will be described.

The key intermediate in the synthesis was the fluorenylidene ketene cycloadduct of 2,3 dihydrothiophene. The cyclobutanone possessing a positive charge stabilizing group at C 3 underwent regioselective 8-ring opening under acidic conditions followed by dehydrogenation with 2,3-dicyano 5,6 dichloro benzoquinone (DDQ) to give Fluoranthено[3,2 b]thiophene

which exhibited a uv/visible spectrum very similar to that of benzo[b]fluoranthene. The preparation of Fluorantheno[1,2-b]thiophene was based on the regiospecific α-ring opening with potassium hydroxide to give a carboxylic acid. Most efficient dehydrative cyclization (orthoannelation) was effected by treating a neat sample of the carboxylic acid with polyphosphoric acid to give dihydrothiophene. Then DDQ was applied for dehydrogenation to produce the desired linear-fused thiophene which exhibited a uv/visible spectrum very similar to benzo[a]fluoranthene.

Spectroscopic data used for their structural assignments will also be discussed.

D4

FLOW INJECTION PRECONCENTRATION/DIRECT SAMPLE INSERTION FOR TRACE ANALYSIS BY ICP-AES AND ICP-MS

P. Moss* and E.D. Salin, Department of Chemistry, McGill University, 801 Sherbrooke St. W., Montreal Quebec, Canada H3A 2K6*

INTRODUCTION

It should be possible to improve the analysis of trace elements by ICP-AES and ICP-MS in several matrices by a combination of flow injection analysis (FIA) and a direct sample insertion (DSI) introduction system. The FIA system allows for sample pretreatment (including the removal of interferents) and preconcentration of the elements of interest. This results in high sample throughput, reduction of matrix effects and lower detection limits. DSI provides two important advantages; (1) higher signal levels (better detection limits) and (2) time resolution of various elemental species (reduction of matrix effects).

Preconcentration chemistries

Ion-exchange preconcentration has proven to be useful for increasing the sensitivity of trace metal analyses as well as reducing matrix interferences. Riley and Taylor (1) first used Chelex-100 in 1968 for the analysis of seawater as did Kingston et al. (2) in 1978 in a column mode. The flexibility of Chelex-100 was demonstrated by Marino and Ingle (3) in the removal of interferents for the analysis of cobalt and by Jones et al. (4) in their analysis of plant and animal tissues.

The first demonstration of the use of microcolumns of Chelex-100 in a flow injection system was by Olsen et al. (5) for the analysis of heavy metals in polluted seawater in 1983. The most detailed method which uses flow injection analysis, with an on-line Chelex-100 column, as a sample introduction system for ICP-AES is that developed and then optimized by Hartenstein et al. (6,7).

There have been several alternatives to Chelex-100 with acid elution proposed recently. Liu and Ingle (8) have tried other complexing agents as stripping reagents for the Chelex-100 to avoid swelling problems associated with its use. The choice of complexing agent must meet two criteria; (1) they must form stronger complexes or chelates with the metals than the Chelex-100 and (2) the complex must be formed rapidly in order to be effective in the time frame of an FIA system.

A novel approach to preconcentration which has recently been introduced by Ruzicka (9) is one that combines column operation with solvent extraction principles. Instead of using an organic solvent for extraction of the metal, a hydrophobic sorbent in a column, in this case C-18 on silica, is employed. A metal chelate is first formed by reacting the metal with a suitable chelating agent such as diethyldithiocarbamic acid (DDC), 8-hydroxyquinoline, pyridylazonaphthol (PAN) or 4-(2-Pyridylazo)resorcinol (PAR). The metal chelate is then introduced to the column where it will be adsorbed onto the hydrophobic surface of the column material. The preconcentrated chelate can then be eluted into a small volume of methanol or other water miscible organic solvent and introduced into a suitable detection system.

A flow injection system has been developed in our laboratory based on a Lachat injection valve. The configuration of the system was altered, ie different columns, connections and sample solutions to test each of the three main types of preconcentration chemistries presented above. Software has been developed to allow computer control of the pumps and valves with the necessary flexibility to allow easy changeover of methodologies. An automated system will provide the precise fluid control necessary for an effective interface to the DSID.

DSID /ETV systems

There are several direct sample insertion devices available for use in conjunction with liquid samples. These include graphite electrodes of varying dimensions and designs (10) including most recently thin walled cups that use inductive heating (11). Wire loops, of either tungsten or tantalum have also been used as sample supports with a detection limit improvement on the order of 10 (12,13). As an alternative to DSID, several investigators have proposed using external electrothermal vaporization (ETV) of the sample before introduction into the ICP (14,15).

The interface problem involves the drying of fairly large sample volumes (approx. 100 uL) that are eluted from the FIA system. This necessitates external drying as opposed to the drying under the plasma that has been used before (12,13). Several drying schemes have been developed for the various devices available and will be presented here along with preliminary detection limits achieved using a graphite insertion probe.

EXPERIMENTAL

FIA System

The FIA system was developed using a Lachat dual injection valve, which included two standard six-port valves, several peristaltic pumps (Minipuls and Alitea C4-V and C6V) and Micro-Line tubing of the appropriate diameter (0.51mm/0.76mm/1.5mm i.d.) which was used for all connections. The other details of the manifolds are given below. A THERMO JARRELL-ASH ICAP 61 direct reading spectrometer was used as the detector in all cases. The parameters used for the analyses are as follows:

Torch Ar flow: 19 L/min
Sample gas flow : 1 l/min (120 psi on regulator)
Auxiliary flow: 0.7 L/min
Forward power: 1.5 kW
Nebulizer: Legere #4 with spray chamber and baffle.

Chelex-100 with acid elution

The Chelex-100 (100-200 mesh) was placed by syringe into a microcolumn (2.3 mm id, 2.0 cm in length) made of tygon tubing similar to that used by Hartenstein et al (6). The Chelex-100 was first changed to its NH_4^+ form by the method suggested by Marino and Ingle (3). The Lachat valve was used in the FIA manifold to load a specified sample volume (1.0 mL and 5.0 mL) onto the Chelex-100 column. A Gilson Minipuls pump was used for the buffer (0.5 M ammonium acetate pH = 9.0) flow at a flow rate of 2.0 mL/min. The sample, 1.0 ppm Cu, Cd and Zn, that was loaded into the sample loop and the acid used for elution (2.0 M HNO_3) were delivered by the Alitea C6-V pump. In this experiment the sample is loaded onto the Chelex-100 column in one direction and eluted off in the other in order to overcome some of the swelling problems of the Chelex. The column was first conditioned by alternately running acid and buffer through it. The sample was loaded into the sample loop during this time. The sample was then loaded onto the column. The sample was then eluted with acid and nebulized into the ICP.

Sorbent Extraction

The column used is available commercially and contains 100 mg of C-18 attached to silica particles packed into a column of 5 mm id and 6.5 mm long.(Bond-Elut C-18 Analytichem International). The sample solution used was 1 ppm Cu and Pb (prepared as above). Various organic solvents were used as eluants including ethanol,

methanol and isopropanol. The column is first treated with the appropriate organic solvent to activate it. The sample is injected by the first valve and reacted with either a reagent stream of 0.05% Na(DDC) or a saturated solution of 8-hydroxyquinoline in 0.01M HAc/0.02M NH_4OH.

The samples were collected, after the injection of the eluant, in 1.0 mL aliquots and then diluted to 5.0 mL with distilled water so as to present the ICP with a 20 % solution of the organic solvent. It is difficult to maintain the plasma while aspirating undiluted organic solvent. A breakthrough sample was also collected as the sample was reacted with the chelator and passed onto the C-18 column. Solutions of the original 1 ppm Cu and Pb samples were prepared in the appropriate organic solvent to give a signal for the samples before treatment by FIA.

Chelex-100 Without Acid Elution

Altex microbore glass columns (3mm id x 50 mm) supplied by Beckman were filled with 100-200 mesh Chelex-100 in the NH_4^+ form. Two different chemistries were investigated using the indicated manifold. The first experiment studied the effectiveness of EDTA as the stripping reagent. The list of reagents required for this run are as follows:

The carrier (C) = 5 x 10-3 M NH_4Ac/1.7 x 10-3 M HAc at pH = 5.2

The stripping reagent (SR) = 0.025 M EDTA at pH = 8-9

The resin regeneration (NH4OH) = 2 M NH_4OH ($NH_3.H_2O$)

Sample solution: 200 ug/L Cd and Pb.

L-cysteine was also tested using:

C = same as above

SR = 0.01 M L(+) cysteine hydrochloride in 0.5 M at pH = 9.2

NH4OH = same as above

Sample solution: 200 ug/L of Cu

The analytical grade chemicals for the reagents are all provided by the Aldrich Chemical Co. Appropriate dilutions of the Fisher-Scientific 1000 ppm stock solutions in 0.01M HNO_3 were used to make the sample solutions.

DSID

To date, an undercut graphite electrode, SPEX 4002, of a 4 mm cup diameter has been used as an insertion probe. It was able to accomodate a 100 uL sample volume, this is on the order of that expected to be delivered from the FIA system after preconcentration. The samples were dried in a brass holder on a hot plate at 75-80 degrees Celcius. The stepper motor run DSID has been described exhaustively elsewhere (13). The only modification made was in the electrode holder which consists

of two 8-32 screws glued into either end of a 3.5 cm. boron nitride rod (5 mm o.d.). A hole was drilled into one end of the graphite cup to allow it to be attached to one of the screws. The spectrometer used was a THERMO JARRELL-ASH multi channel with software and hardware modifications made by Technical Services Laboratory (16).

RESULTS AND DISCUSSION

Flow Injection Systems

The preconcentration values for the three chemistries attempted were calculated by comparison of peak heights obtained before and after as measured in intensity units. The results are given in the tables below:

Table 1 Chelex-100 With Acid Elution Results

Sample Loop	Metal	Intensity I_1	Intensity I_0	Preconcentration Factor (I_1/I_0)
1.0 mL	Cu	6011	721	8.3
	Cd	4878	760	6.4
	Zn	5392	696	7.7
5.0 mL	Cu	23881	721	33
	Cd	16379	760	22
	Zn	16337	696	24

Table 2 Sorbent Extraction Results

Metal	Chelator	Eluant	Intensity Reading Corrected I_1	Intensity Reading Solvent I_0	Preconcentration Factor I_1/I_0
Cu	8-HQ	2propanol	8014	594.6	14
Cu	8-HQ	ethanol	7742	483	16
Cu	NaDDC	methanol	6483	974	7
Pb	8-HQ	2propanol	1936	69.9	28
Pb	8-HQ	ethanol	2507	85.7	30
Pb	8-HQ	methanol	1527	229.5	7

Table 3 Chelex-100 Without Acid Elution Results

Stripping Reagent	Metal	Intensity I_1	Intensity I_0	Preconcentration Factor (I_1/I_0)
EDTA	Cd	4337	179	24
	Pb	3087	19	22
L-cysteine	Cu	8216	164	50

The best results were obtained using L-cysteine to elute copper. The difficulty with this method is that it is element specific. Chelex-100 with acid elution provides the most universal technique that can be applied to a large variety of metals. The problem we foresee with an acid eluant is the effect it may have on the wire loop of tungsten should we decide to use it as the DSI of choice. The sorbent extraction may well be a suitable alternative to Chelex-100 but its full potential has not yet been explored.

DSID

Only preliminary investigations have been completed using the graphite insertion probe described previously. The experiment was not optimized for important factors such as insertion height. The effect this has on signal intensity and plasma shape has been shown by Shao and Horlick to be a crucial issue (10). The detection limits obtained for several elements with this unoptimized DSI system are given in Table 4. We have also included an estimate of detection limits calculated by considering the preconcentration factors found by FIA as divisors.

Table 4 Estimated Detection Limits

Elements	FIA Method	Factor	Detection Limits (ppm) DSID	Detection Limits (ppm) Estimated
Cd	Chelex 100	22	0.1	0.005
Pb	Sorbent	30	0.5	0.017
Cu	L-cysteine	50	0.2	0.004

CONCLUSION

We have shown by experimentation that there are a number of FIA chemistries easily capable of producing preconcentrations in the range of 10-20. Our future efforts will be directed toward the search for a suitable interface and methodology for drying and vaporizing the sample. We will continue to explore DSI techniques and will move into the new area of electrothermal vaporization which appears to offer some advantages.

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D5

HOT SLURRY SAMPLE INTRODUCTION FOR ICP-AES

Eric D. Salin*, Lyne Gervais, Laurie Usypchuk, Department of Chemistry, McGill University, 801 Sherbrooke St. W., Montreal, Quebec, Canada H3A 2K6

INTRODUCTION

Inductively Coupled Plasmas have traditionally been used for the analysis of liquid samples, but the development of the Babington or high solids nebulizers offered a simple approach to the analysis of solid samples. The slurry technique uses those nebulizers for the nebulization of suspensions of finely ground material. The slurry technique has been applied to the analysis of samples such as coal, kaolin, biological and agricultural materials. In most of those analyses, the major and minor elements were of interests and were determined with good accuracy.

The determination of analytes at the trace and sub-trace levels is more difficult with the slurry technique. One limitation comes from the efficiency of transport of the system. As with most traditional nebulizers, the efficiency of the high solids nebulizers results in the introduction in the plasma of about 1% of the original sample.

The analysis of materials such as sediments, soils and rocks by the slurry technique gives inaccurate results. The problem comes from the difficulty of breaking down the particles in the plasma. In general, particles of less than five microns are required for the slurry technique to work properly. But with many materials, for example alumina, smaller particles must be used to have complete break down in the plasma. The grinding period necessary to achieve these particle sizes can be so long that all advantages of the solid sample analysis method are lost.

Two sample introduction systems were studied as possible ways of overcoming those limitations of the slurry technique. A first system was designed to work on the transport efficiency problem. A heated spray chamber evaporates the solvent which is then removed by a condenser. Reduction of the droplet size is expected and should result in an improvement of the transport efficiency since the size of droplets is the primary factor controlling the transport process.

The second system uses a flame to introduce the sample into an expansion chamber. The aerosol travels through a condenser, which removes the excess solvent, before being introduced in the plasma. A total consumption burner with an hydrogen/oxygen flame was used. The high efficiency of this burner should result in an

increased efficiency of the transport process but more interesting is the possibility of having a preliminary breakdown of the particles. The temperature of a hydrogen/oxygen flame is about 3000 °C which should be sufficient to decompose many materials and to atomize completely others. A preliminary decomposition of the materials should allow larger particles to be used. Since the material should all be in either a vapor or small particle form, transport efficiency should be higher.

The conclusions drawn from the use of those systems for the introduction of slurries into the Inductively Couple Plasma will be presented.

EXPERIMENTAL

Instruments

All determinations were done on a Thermo-Jarrell-Ash ICAP-61. A custom program was used to control the spectrometer when background signals were required for the calculations. Sample was delivered to the nebulizer by a peristaltic pump.

Systems description and operating conditions

The normal sample introduction system for slurry was composed of a Legere nebulizer and a spray chamber with a baffle of the double-pass type.

The Hot Chamber System (Figure 1) used the same nebulizer as the Normal System. The spray chamber is of the same design except for a minor modification in the length and shape of the outlet. A ground glass connector was used to connect the chamber to the coiled condenser. It also provided the proper angle for evacuation of the solid material from the chamber. The chamber and the connector were heated with a heating tape controlled by a variable power supply. The condenser was cooled with tap water run through an ice-water bath providing a water temperature of 8 °C. The temperature of the spray chamber was set at 105 °C which was determined to be the optimum condition for signal-to-blank level.

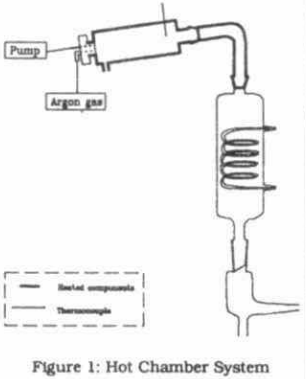

Figure 1: Hot Chamber System

For those two systems, the operating conditions were forward power: 1.0 KW, plasma gas: 16 L/min, auxiliary gas:

0.3 L/min, nebulizer gas: 0.9 L/min and sample delivery rate: 1.9 mL/min.

The flame system used a Gilbert burner to introduce the samples into a glass expansion chamber and a Friedrichs condenser to remove the water. The chamber and condenser were used at the vertical and were attached together by a glass connector. The system was connected to the torch with a Tygon tubing. The injector tube was an alumina tube of 3 mm of internal diameter which was extending up into the lower portion of the plasma.

The burner was operated with 1.5 L/min of oxygen and 3.1 L/min of hydrogen. Argon gas at a flow rate of 1 L/min was added through the burner to carry the aerosol. The sample flow rate was 0.5 mL/min. A 1.75 KW plasma was used while the plasma gas was set at 20 L/min and the auxiliary gas at 1.2 L/min.

Samples and standards preparation

The slurries were made from reference materials: BCSS-1, MESS-1 and PACS-1 from the National Research Council and the NBS1646 and NBS1633a from the National Institute of Standards and Technology. These materials were ground for 30 min with a Spex 5100 mixer/mill in an agate vial. Particles of less than 2.5 μm were obtained in 90% of the sample. The suspension was made by placing 0.5 g of ground materials in a 100 mL volumetric flask and dispersing it in 1.0 M nitric acid. The suspension was magnetically stirred for 5 min and then placed in an ultrasonic bath for 30 min to complete the dispersion.

The liquid standards were prepared from 1000 ppm reference solutions and deionized distilled water. The standard's medium was made to match the content in acid of the slurry.

Procedure for transport efficiency determination

The transport efficiency of the two systems was determined by a filter collection procedure based on that used by Olson et al.[1]. The aerosol coming out of the plasma torch was trapped on a 0.1 μm polycarbonate filter (Nucleopore). A digestion was done with nitric acid and the solutions obtained were analyzed by ICP.

RESULTS

HOT CHAMBER SYSTEM

Signal intensity

The performance of the Hot Chamber System was determined from a comparison of the slopes of its calibration curves with those of the Normal System. For the analysis of slurry samples, the Hot Chamber System increased the background

corrected signals by a factor of 3 (±0.3), on the average. Results for the different samples are shown in Table 1. Meanwhile, the signals for liquid standards were increased by a factor of 11 (±1).

Table 1 Slopes of calibration curves for liquid and solid samples with the Normal and the Hot Chamber System.

Element	Slopes (cts/ppm)					
	Liquid			Slurry		
	Normal	Hot	Factor	Normal	Hot	Factor
Cr	2473	22448	9.1	1738	5175	3.0
	(98)	(254)	(0.5)	(210)	(820)	(0.8)
Mn	3956	47249	11.9	2127	7494	3.5
	(269)	(1373)	(1.2)	(234)	(2053)	(1.3)
Ni	1129	13136	11.6	1788	5310	3.0
	(81)	(206)	(1.0)	(120)	(677)	(0.6)
V	1726	18118	10.5	1142	3583	3.1
	(65)	(222)	(0.5)	(71)	(284)	(0.4)
Zn	2945	29942	10.2	4140	11703	2.8
	(44)	(546)	(0.3)	(64)	(291)	(0.1)
Average			10.7			3.1
Deviation			1.1			0.3

( ) indicates standard error on the slope or the error on the factor.
Slopes of slurry sample were calculated from signal intensities of the different samples analyzed.

Signal stability

The Hot Chamber System initially gave very noisy signals. The flow of the injection gas was affected by fluctuations produced inside the system. This resulted in severe disturbance of the plasma. The flow of gas was fluctuating between being to low to form the central channel and being so high as to bring the tip of the IRZ to the top of the plasma. Displacement of the plasma was also observed.

The diameter and the shape of the injector tube were found to modify the degree of perturbations of the plasma. The normal injector tube of the ICAP-61 system was replaced with a capillary injector tube of 1.0 mm of internal diameter. A smooth flow of injection gas was obtained with this new tube as shown by the stable central channel.

The stability of background corrected signals was calculated as the average of a set of 80 repeats of 10 sec signals. The Hot Chamber System using the capillary injector tube provided about the same stability of signal for liquid samples than the

Normal System did: 1.3 % (±0.2) versus 1.9 % (±0.4). When running slurry samples, the signals are slightly more unstable with the Hot Chamber System. Variations of 2.8% (±0.9) were obtained as opposed to 1.7% (±0.7) with the Normal System.

Table 2 Variations of signals for liquid and slurry samples

	% RSD			
	Normal system		Hot Chamber System	
	liquids	slurry	liquids	slurry
Al	1.4	1.6	-	2.8
Cr	2.3	3.2	1.5	3.4
Fe	1.3	1.1	-	2.9
Mg	1.8	1.3	1.1	1.6
Mn	2.5	1.4	1.2	3.3
V	1.9	1.8	1.5	3.8
Zn	2.0	1.7	1.1	1.6
avg	1.9	1.7	1.3	2.8

Using 80 repeats of background corrected signals of 10 sec of integration.

Transport efficiency

The Hot Chamber System increased the transport efficiency of liquid and of slurry samples by the same factor. The amount of analytes collected from the aerosol of the Hot Chamber System, when liquid samples were run, increased by a factor of 1.9 (±0.4). For slurry samples, the increase was 2.4 (±0.4).

Water loading

The water content in the aerosol of the two systems was determined because of its importance on the plasma conditions. The aerosol of the Hot Chamber System was found to introduce into the plasma 9.3 mg of water per minute. The Normal System generates an aerosol with 16.4 mg of water per minute. A reduction of 38% of the water loading of the aerosol is obtained with the Hot Chamber System.

Accuracy of analysis

The accuracy of analysis of the Hot Chamber System and the Normal System were determined for elements in concentration ranging from the major to the trace level. Liquid standards were used to establish the calibration curves. The percent recovery of each analyte was calculated as the ratio of the concentration determined with the system to the concentration certified by the supplier. Table 3 shows the results of the different elements and samples analyzed for the Hot Chamber System and the Normal

System. The Normal System provides somewhat low results but the Hot Chamber System is very inaccurate. The minor and trace constituents show less than 50% recovery. The recovery of the Hot Chamber System is, on the average, 3.3 (±0.9) times less than that of the Normal System. This difference correlates with the discrepancy in signal increase between the liquid and solid samples obtained with Hot Chamber System: 3.4 (±0.7).

Table 3 Recovery for the analysis of slurry samples with the Hot Chamber System and the Normal System.

	BCSS-1		MESS-1		PACS-1		NBS1646		NBS1633a	
	N	H	N	H	N	H	N	H	N	H
Fe	89	78	76	70	80	54	89	69	39	30
Mg	79	58	69	62	72	47	85	65	65	42
Co	-	29	-	17	-	36	-	12	67	18
Cr	76	36	43	31	60	22	75	34	67	27
Cu	-	57	-	46	98	38	-	47	61	26
Mn	81	29	63	20	75	17	78	21	19	12
Ni	106	33	62	22	98	24	86	23	64	17
Pb	-	-	-	-	98	26	-	-	-	-
V	101	34	76	26	90	20	92	26	75	21
Zn	92	25	96	27	135	35	111	23	63	15

Recovery reported in % of the certified concentrations.
'–' indicates an impossibility of determination due to too low a concentration.
N Normal System
H Hot Chamber System

FLAME SYSTEM

The condensation efficiency of the desolvation stage is very high, about 99%. Even though a small amount of water is introduced in the plasma, it is very difficult to maintain the plasma. Changing the injector tube to one of a larger diameter (3.0 mm) and inserting it into the plasma (5 mm above the load coil) allowed the flame system to be interfaced with the plasma. With this configuration, good stability of signals was obtained: 2%.

The flame system can be used to nebulize slurry samples of 0.5% w/v with no clogging problems but the transport efficiency is not better than that of nebulizer/spray chamber system. The detection limits of this system are not expected to be lower than for a nebulizer system. Memory effect is a serious problem with this system. A flush

time of a minimum of 2 min is necessary because of the length of the system but also because of deposition on the walls of the expansion chamber.

CONCLUSION

The Hot Chamber System provided an improvement in transport efficiency as expected. The increase resulted from the evaporation of water from the droplets. The size of the particles included in the droplets and the efficiency of transfer of heat to the droplets are two factors limiting the improvement of the transport efficiency. Therefore, it is probably impossible to increase the transport efficiency by more than a factor of two with a system of the type of the Hot Chamber System.

As shown by the increase in signal intensity, the transport efficiency is not the only parameter involved in the performance of the Hot Chamber System. The signal intensity of slurry samples is increased by three when there is only twice as much analyte introduced in the plasma. So, other factors must be affecting the signal intensity. This becomes obvious when considering the signal increase produced by the Hot Chamber System for liquid samples. The additional factor of signal increase is attributed to changes in the plasma conditions.

The difference in the amount of water introduced in the plasma could generate different conditions. The temperature of the plasma could be lower with the Normal System since more water has to be evaporated and atomized. Also, the Hot Chamber System generates an aerosol containing more water vapor than the Normal System. Since water vapor is known to produce a reduced cooling of the plasma[2], this difference in the composition of the aerosol could also contribute to an alteration of the plasma conditions.

Modifications of the plasma conditions could be responsible for the signal increase but also for the poor accuracy of the Hot Chamber System. The low accuracy is a consequence of the discrepancy in signal intensity obtained for solid samples and liquid standards. This seems to result from a difference in atomization efficiency of the plasma for the two types of samples. The reduced availability of water in the plasma reduces the supply of hydrogen and oxygen and both components are contributing to the transfer of energy between the plasma and the particles[3]. A change in the plasma composition, of both hydrogen and oxygen, could affect more severely the decomposition rates of the solid particles than the atomization of liquid samples since much more energy is necessary for the first process.

The Hot Chamber System resulted in an increase in transport efficiency but other parameters are simultaneously modified such that the system gave poorer performance for the analysis of slurry samples. Meanwhile the results for the flame system did not demonstrate any increase in transport efficiency or particle breakdown. The results of these two projects tend to show that the accuracy of analysis by the slurry technique is controlled by the energy available for the different processes occurring in the plasma. Overcoming the limitations of the slurry technique might therefore be possible with the modification of the chemical environment of the plasma.

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D6

FLOWING STREAM MICROWAVE SOLID SAMPLE DECOMPOSITION

Eric D. Salin* and Fu He Li
Department of Chemistry, McGill University, 801 Sherbrooke St. W. Montreal, P.Q., Canada H3A 2K6, Phone: (514) 398-6236

Microwave aided digestion offers significant speed advantages over conventional atmospheric or bomb digestion techniques for certain sample types [1-4]. It is our plan to develop a flowing stream microwave system suitable for the digestion of solid samples. We expect that such a system would provide the power of microwave digestion with the convenience of flow injection type sample handling. In addition, automated handling of liquids should minimize the fume and handling hazards which can result when using the more powerful reagents required for some difficult digestions.

We have previously reported that a prototype of our microwave system was capable of digesting a copper ore sample in several minutes (©1988 MOE Technology Transfer Conference). This indicates that energy is coupled successfully to the tubing inside the microwave oven. Our pressure-temperature data from those experiments (Figure 1) show that higher pressures and temperatures are reached than those obtainable at atmospheric pressure.

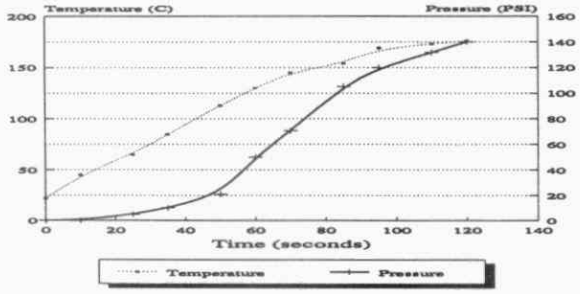

Figure 1. Temperature and pressure inside microwave tubing

Our proposal involves the development of a major segment of Figure 2.

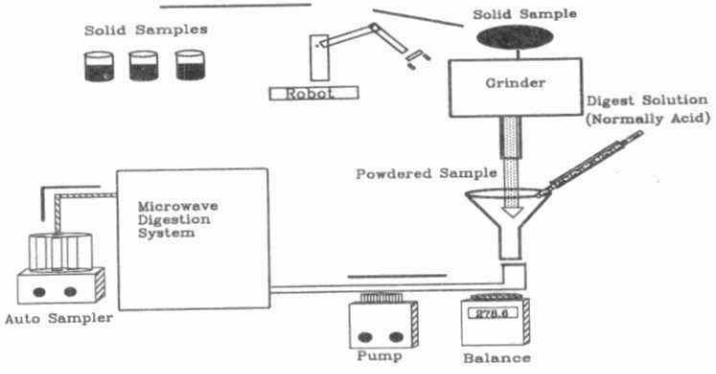

Figure 2. Total system for microwave solid digestion

We are interested in the process from the funnel through the microwave digestion process. Our plan primarily revolves around development of the microwave system itself, as illustrated in Figure 3.

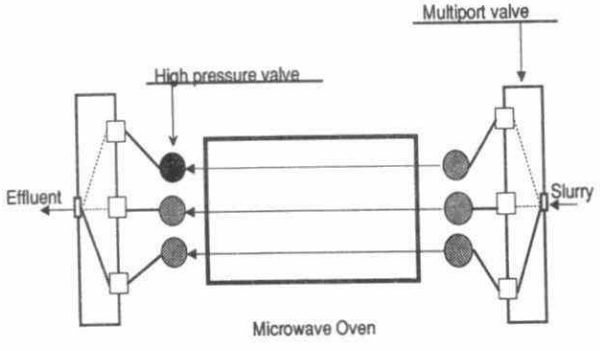

Figure 3. Continuous asynchronous system

At this point we are building a single tube electrically controlled system such as that illustrated in Figure 4. If the single tube system works well, then a simple modification will provide the multi tube system illustrated in Figure 3. It appears to us now that the system in Figure 4 offers considerable potential from the liquid handling point of view. We have, for convenience, shown the solid sample as being supplied by an autosampler. A configuration of this type will allow a variety of acids to be mixed in virtually any proportion. It would be possible to mix the acids directly in tubing by rapidly switching between acids and letting the segments mix in a mixing coil, however we feel that the simplicity of the chamber is superior at this stage.

Our experiments to date have brought up some interesting problems. We will address the problem and then a possible solution (when available) in the text below.

1. Problem: Sediment left in tubing.

Actually, the major problem here seems to know if there is sediment in the tubing. Since the tubing can be made of a variety of materials, including low friction compounds like Teflon (as a lining), the sediment can probably be rinsed out with a high velocity flush. Sediments would offer the potential for contamination of the following samples. Unless prior knowledge suggests complete decomposition, a flush may be essential as part of the normal operating mode. The time required would be short.

2. Problem: Bubble formation.

We have had bubbles appear during our copper ore experiments. One must realize that the exhaust valve is opened before the inlet valve. This releases the pressure to atmospheric levels and may cause the release of additional bubbles. To date, they have not been a problem. The higher pressure in the tubing does cause an outward flow from the system, but this is expected. The wash of new material coming in seems to pick up all bubbles when 0.25 in i.d. tubing is used. A flush cycle, as suggested above, would almost ensure bubble removal.

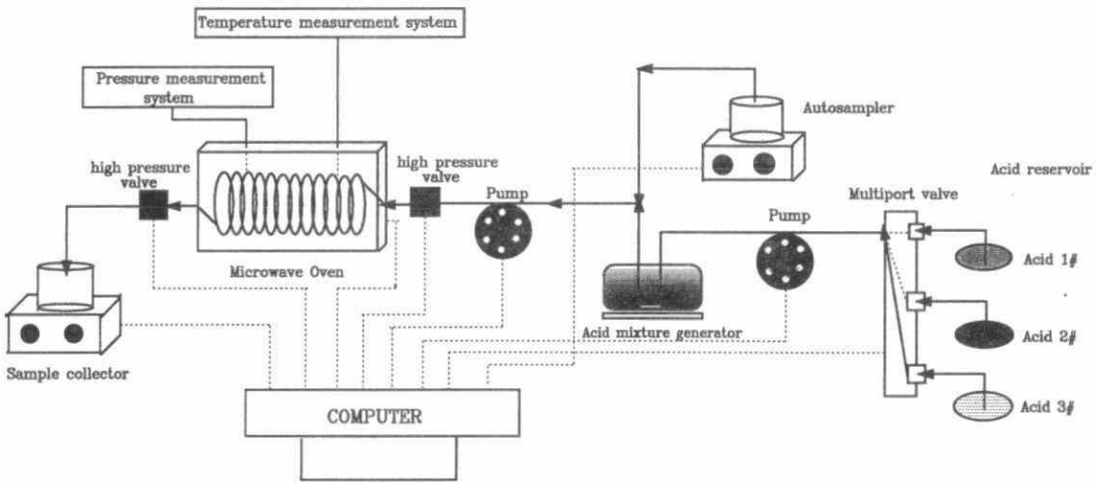

Figure 4. Automated Flowing Stream High Pressure Microwave Sample Digestion System

3. Problem: Radiation leakage.

Since acidic solutions can be charge carriers (conductors) there is some concern that tubing emerging from the microwave oven would act as an antenna. There are several solutions to the problem. The first is to seat the high pressure valves on the walls of the oven. We have done this and observed no measurable leakage using a sensitive detector. Another solution is to use air bubbles at the ends of the solution segment. Our data with various volumes of bubbles (Figure 5) suggests that heating is independent of bubble volume.

4. Problem: Particle flow from the system.

For atomic analysis, this is a problem only if the particles are too large to run through a high solids nebulizer for atomic analysis. This would place them larger than 5 to 10 microns in size, depending on the nature of the material. This may require a detector on the flowing stream for larger particles (5 microns and greater) and either a recycle capability (feedback loop) or a warning to the operator to examine the sample or resubmit the sample for further digestion.

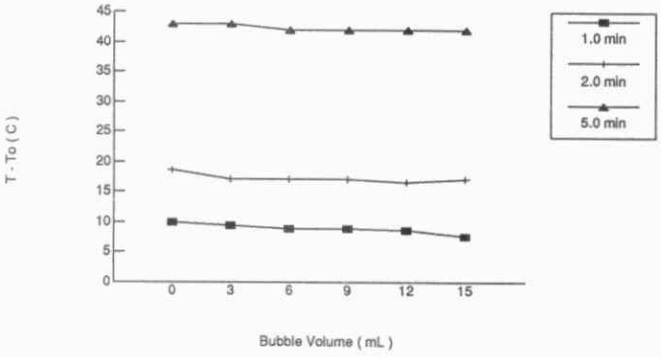

Figure 5. Temperature and Bubble Volume for different heating times.

5. Problem: Temperature measurement

Control of the temperature and pressure during the digestion is critical to the efficiency, reproducibility and safety of the procedure. Temperature measurement is complicated by the high energy microwave field in the cavity. Conventional thermocouple devices can not be directly used in this environment. If a bare wire thermocouple is introduced into an operating microwave oven, electrical discharges (arcing) will typically be observed. These can be sufficiently severe as to destroy the thermocouple or even the oven. Meanwhile, a large quantity of microwave energy will be transported out of the cavity. Large currents are also induced in the thermocouple wires leading to spurious signals which then swamp out the thermally induced voltages of interest. This problem has been solved with a well shielded and grounded metal cable (Figure 6) which can shield successfully the thermocouple wires from microwave field.

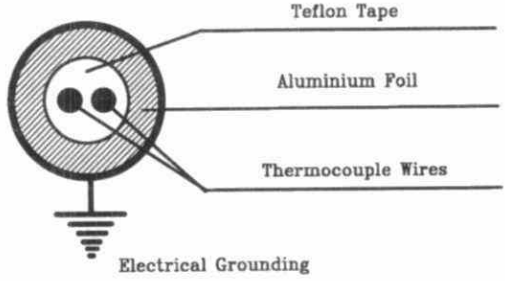

Figure 6. Schematic diagram of the metal cable

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Solid Sample Insertion with Pellets for ICP-AES and ICP-MS

Eric D. Salin and Laurent Blain*
Department of Chemistry, McGill University, 801 Sherbrooke St. W., Montreal, P.Q., Canada H3A 2K6

INTRODUCTION

The analysis of many materials remains a difficult challenge for the analyst. Chiefly, the difficulty lies in the conversion of the material as it occurs naturally to a form suitable for analysis by the instrumental technique of choice. Many materials of interest to environmental scientists occur naturally as solids, two common examples are vegetation and sediments. In this cases, the solid must be dried, ashed and ground, and the resulting powder is then decomposed either by an acid digestion or an alkali fusion. Acid digestions are often complicated by the contradicting solubilities of elements of interest, so that they typically involve a sequence of filtrations and dissolutions. In short, the conventional sample preparation procedures are often very time consuming and demand skill on the part of the analyst.

An attractive alternative would be to bypass the reduction of the powder to a liquid form, and insert it directly into the plasma[1,2,3,4]. Some preliminary results for the direct insertion of powdered samples in a graphite cup into the plasma have been very promising[1,2]. We have already reported how directly pressing a graphitic material into a pellet resulted in an improvement of detection limits commensurate to the increased mass of sample thus inserted in the plasma[1]. For example, we have brought the detection limit for lead in g-standards from about 1 ppm with a graphite cup down to about 0.1 ppm with a pellet by ICP-AES, and down further to 0.02 ppb by ICP-MS. These concentrations fall below the levels found in three sediment reference materials, MESS-1, BCSS-1 and PACS-1 (NRC Canada), and suggest that the analysis is feasible, in terms of detection limits.

In this report, we will present work that is currently being pursued in our laboratory to apply this technique to the direct analysis of sediments. The emphasis will be on the factors that affect the volatilization of various classes of elements from the probe, because ultimately it is that step which limits the applicability of this technique.

EXPERIMENTAL

Instrument

A direct reading spectrometer, modified by Guy Legere of Technical Services Laboratories, was used to collect all of the data that will be presented in this report. This instrument has already been briefly described in earlier presentations and a recent publication[1]. In short, the operation of this instrument has been put entirely under the control of a microcomputer, so that many of the limitations of conventional direct readers for the acquisition of transient signals are lifted[6]. Table 1 lists the plasma operating conditions and observation parameters.

Procedure

The solid standards that were used in this experiment were the SPEX g-standards, for the work with graphitic matrices, and for the work with sediments it was PACS-1, a sediment reference material from the NRC (Canada).

A hand operated briquetting press, commonly used in calorimetry, was used to prepare the pellets. Although the g-standards could be directly pelletized, it had already been reported that geological samples will melt or sinter into a refractory globule if they are inserted directly into the plasma with a graphite cup, and that prior mixing with graphite is essential[4]. Furthermore, it is impossible to pelletize the sediments with a hand operated press unless they are mixed with graphite in a proportion of at most one part sediment to one part graphite. The relevant data on the equipment and reagents that were used in these investigations are compiled in Table 2.

RESULTS AND DISCUSSION

Preliminary investigations with sediments

Pellets pressed from a mixture of sediments in graphite were more difficult to insert directly in the plasma than the g-standards had been. Unless the insertion is slow and gradual, the violent release of gas that results will extinguish the plasma. After a few seconds the bright orange emission of silicon fills most of the plasma's body, this is accompanied by a sharp increase of the reflected power and an audible rumble from the plasma. This silicon emission can last longer than five minutes for a one to one sediment mixture, at relatively low insertion depths. Next, a bright blue emission takes over the upper cone of the plasma, and it is soon surrounded by pink and purple emission from calcium, and the base of the pellet is sometimes surrounded by the green emission of carbon. This sequence is illustrated in Figures 1-a) through 1-d) for various insertion depths, and dilution ratios of sediment in graphite.

A pre-heat step at the base of the plasma provides the best signals for the volatile elements, such as arsenic, Cd, Pb and Hg. These signals are smooth narrow peaks, with little tailing. On the other hand, if the probe is pushed slowly into the plasma without a pre-heat step, the signals for these elements progress as the plasma is upset by the sudden release of large quantities of gases generated by the thermal decomposition of the sediment's matrix. This, in turn, leads to weaker signals that are spread out and noisier, often the peaks are replaced by two or more bursts.

If the pre-heat position is close enough to the base of the plasma, some silicon emission is eventually observed as the tip of the pellet gets hot enough to glow. At this point the probe can be pushed deep into the plasma without extinguishing it, by then the matrix of the sediments has been reduced to its more refractory components and will not expel much more gas when the temperature of the probe is raised. The probe must be pushed quite deep into the plasma, otherwise it will be surrounded by a sheath of silicon vapor that will shield it from the plasma, as in Figures 1-b) and 1-d). The signals of elements of intermediate volatility, which appear at about the same time as the silicon emission, confirm the formation of an insulating sheath around the pellet. For example, Fe and Mn start coming off at about the start of the silicon emission but fall down to their baselines as the silicon emission grows in intensity, and resume as the silicon emission dies out.

The signals of more refractory elements, such as Co and Cr, are often difficult to discern because they are usually broad, quite weak, and do not stand out well against their very intense drifting baselines. The data acquisition procedure can be adapted to enhance the resolution of these signals from their baselines, by delaying the start of the observation period and keeping the integration times small. However this does not improve the quality of the signals themselves, which remain extremely spread out.

Volatilization mechanisms

The poor signals of the refractory elements were not surprising, these elements had also resulted in poor signals with the simple g-standards. With graphitic matrices, it has become common practice in the DSI literature to ascribe the absence of signal from refractory elements to the formation of their even more refractory carbides[2,5]. And indeed, the work of arc spectroscopists in the early nineteen sixties supports this conclusion in many instances[7,8,9]. Drawing from the experience of arc spectroscopists, some workers have investigated the applicability of thermochemical additives to enhance the volatilization of selected elements[2,5]. For example, Mo forms a very refractory carbide and usually no signal is observed for this element, but when either Teflon or NaF is added to the sample a sharp well defined peak is recorded for this element.

This solution is not universal however, as with any chemical reaction the formation of a volatile compound of the element depends on the free energy of its reaction with the additive. Thus, the reagent that results in one hundred percent recovery of one element may not do much for another. For example, NaF does not result in any noticeable improvement of the signal of Cr and Fe, among others, and for Fe it is already known that a better choice would be AgCl[5].

The choice of a volatilization enhancer must be based on an approximate knowledge of the thermodynamic and kinetic parameters of the thermochemical reaction. It is often difficult to find suitable values for the latter, particularly at temperatures found in the ICP. Furthermore, the assumptions made in the derivation of the temperature dependence of free energies are often stretched for temperatures so far removed from the standard state. Nevertheless, these thermodynamic calculations have been successfully used by arc spectroscopists to study the formation of carbides in graphitic matrices[8], and have been useful in understanding the effect of the two thermochemical additives investigated here, NaF and AgCl.

As a general rule, when the boiling point of the relevant halide of the element of interest is well below that of the additive, the kinetics of the thermochemical reaction often have little impact on the enhancement of the signal. As the boiling point of the reaction product increases towards that of the additive, the insertion procedure must be adjusted so that the temperature of the probe does not rise too quickly or the reagent will boil off before the reaction can proceed. For example, the boiling point of CrF_2 is separated by less than 300^{o}C from that of NaF and its signal is not significantly enhanced by the presence of this additive, on the other hand MoF_6 has a boiling point about 1600^{o}C lower than that of NaF and its signal is dramatically enhanced by the presence of the latter. However this rule does not apply in many instances, for example it does not explain the different effect of AgCl on Co and Fe. The boiling points of the relevant chlorides of these two elements are not very far apart, yet the signal of Co is only enhanced by the presence of AgCl in the reaction mixture if a pre-heat step preceedes the insertion of the pellet deep into the plasma, while the signal of iron is always improved by the presence of AgCl in the reaction mixture.

Matrix effects

The most striking difference between the g-standards and the sediment reference materials, in terms of their analysis by DSI, is the presence of large concentrations of silicon in the latter. It has already been noted how a very bright silicon emission is observed in the whole body of the plasma after the pellet has been inserted into the plasma, and how the signals of Fe and Mn fall back to their baseline during its peak. This matrix effect must be considered from two perspectives, on the one hand the effect of large masses of silicon released at once in the plasma must be ascertained, and on the other hand its effect on the physical and chemical conditions in the probe must be investigated.

To study the influence of large masses of silicon on the excitation conditions of the ICP, segregated pellets were prepared where one layer of the pellet was composed of a mixture of g-standard in graphite and another was composed of SiO_2 in graphite. The slope of the calibration curves obtained with these pellets were compared with that from pellets of mixtures of g-standards in graphite only, and no significant difference was observed. This result agreed with what others have reported[2] for synthetic standards similar to the g-standards where the matrix is not graphite but silica. Thus, the loss of signal for Mn and Fe cannot be attributed to changes in the excitation conditions in the plasma. Although these segregated pellets caused a bright orange emission, they did

not disturb the plasma as much as the sediments did, probably because the latter also release a lot of gas when the rest of their matrix decomposes, which may push the plasma upwards and temporarily move the zone of maximum emission out of the spectrometer's view. To investigate this last possibility, the orientation of the segregated pellets in the plasma was varied, so that sometimes the SiO_2 would be on the bottom and sometimes on top. It was observed that when the silica layer is the bottom the slope of the calibration curves are noticeably shallower than when it is on top, which accords with the observation that if the sediment pellets are not pushed deep enough into the plasma the bright white core stays above the pellet and does not close under the pellet until the orange emission is virtually over.

The observation that the excitation conditions are not affected by the presence of silicon means that it does not cool the plasma, so that the effect of silicon on DSI must be studied at the pellet plasma interface and in the pellet itself. It is clear that the insertion parameters must be adjusted to allow the plasma to reshape under the pellet, so that the emission zone of the refractory elements does not get temporarily pushed up and out of the observation zone of the spectrometer. It is still possible that the streaming silicon vapor will insulate the pellet from the hot core of the plasma and thus keep its temperature fixed at the boiling point of silica during that period. It is also possible that melting silica forms a network of refractory globules in the pellet[4], and varying the dilution ratio of the sediments in graphite should provide a clue as to the severity of this effect. The data collected so far does not provide a firm clue as to whether this last effect is significant and whether it is relieved by further dilution of the sediments in graphite. Likewise, because the thermochemical additives that are used to enhance the volatilization of the refractory elements can also react with silica, in effect acting as matrix modifiers, it is difficult to discern whether their use is advantageous at this time.

Electrothermal vaporization (ETV)

The applicability of a thermochemical analysis of the volatilization mechanisms with pellet DSI is limited by the lack of control over the temperature of the pellet in the plasma. The only parameter that has a direct effect on the temperature of the pellet is its position relative to the plasma, however the heat gradients under the base of the plasma and in it are so steep that the temperature accross the length of the pellet probably ranges over several decades. Thus, adjusting the kinetics of the thermochemical reactions that result in volatilization enhancement by varying the

pre-heat height and the insertion depth remains a empirical endeavour. Clearly, at this stage, it would be helpful to devise a technique that allows the verification of the thermochemical calculations and the identification of the volatilization mechanism for groups of elements so that the true potential of volatilization enhancers can be established. This information could in turn be used to advantage in the optimization of the insertion procedure.

Work has begun on the development of an electrothermal atomization device that accomodates the pellets of DSI, and the preliminary results are encouraging. The basic idea has already been described[10], in this instance we have replaced the graphite tube of the furnace of a Perkin Elmer HGA 2200 with a pellet. The vaporized sample is swept into the plasma by a flow of argon, through the injector tube of a standard torch. The signals obtained with this arrangement are easier to discriminate from their simpler baselines. Thus, the signals of cobalt and chromium that are measured with the ETV system are easier to discern than those that are obtained with DSI. Some initial very rough detection limits fall in the hundreds of parts per billion, they will surely be improved by a better design of the ETV chamber.

The full potential of the ETV approach may only be realized when the heating ramp is used to selectively volatilize the elements with low boiling points, then drive all the silicon out of the pellet by keeping the temperature at silicon's appearance temperature, and finally ramp the temperature up again to volatilize the refractory elements. The three phases are made independent of each other and the observation parameters, such as the integration time, can be systematically optimized for each individual element because its appearance time is determined by the temperature program. A further advantage of ETV is that it allows much higher masses of sample to be used, with a consequent improvement of detection limits and sampling statistics.

CONCLUSION

Our current work with pellet DSI is concerned with establishing to a first approximation what the particular volatilization mechanisms are for a group of representative elements, and how this information could be used to enhance the signal of classes of elements and minimize matrix effects. Concurrently, we are concentrating on the identification of the matrix effects of the silicate matrix of sediments, from which it will in turn be possible to design an adequate calibration procedure for pellet DSI.

The ETV experiment holds great promises in that direction. First, because it provides control of the pellet's temperature, which is essential for thermodynamic and kinetic investigations. But also, this control over the kinetics of reactions in the pellet introduce the possibility of directing the thermochemical reaction in the pellet to advantage, and for complicated sample types like sediments, this may well give it the leading edge.

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D8

RETRACTABLE COMPOSITE ABSORBENTS FOR ENVIRONMENTAL CLEAN-UP

B.Gillies*,E.Forsberg, M.Garces, R.Li, L.Read,E.Stubley,
EcoPlastics Ltd., Willowdale, Ontario, M2H 3B4

O.Meresz,
Ontario Ministry of Environment, Rexdale, Ontario, M9W 5L1

INTRODUCTION

In certain Great Lakes areas, clean-up of contaminated sediments in creek, river and lake bottoms is the most pervasive and perhaps most difficult challenge for remediation.[1] Bulk spills from industrial sources into water bodies are major contributors to contaminated water and sediment. The 1985 perchloroethylene spill into the St. Clair River focussed public attention on this problem and on the lack of effective methods for spill clean-up. The most common method for removal of contaminants from river bottoms is dredging. However, this method is contraversial for a variety of reasons, including the generation of a large volume of contaminated waste and the resulting disposal problems.

The Ontario Ministry of the Environment and EcoPlastics Ltd. embarked on a joint development program targetted at the development of an alternative river bottom clean-up method. A method was desired which would reduce the volume of waste generated and which would also minimise the disturbance to the river bottom.

Two approaches were identified for clean-up of contaminated sediments:
i) capture of trace amounts of organic chemicals dissolved in water leaching from the sediment; and
ii) clean-up of bulk spills of organic chemicals.

SEDIMENT CLEAN-UP BY ADSORBENT CONTAINED IN A POLYMER COMPOSITE.

The Ontario Ministry of the Environment expressed an interest in using magnetically retractable adsorbent materials for clean-up of contaminated sediments. This material, combining adsorbent and metal in a polymer matrix could be thrown onto the contaminated sediment, where it would adsorb contaminants from either the sediment or the water above the sediment. The adsorbent could then be retrieved by passing a magnet over the area. An initial program, Project No. 257RR was undertaken to demonstrate the viability of the retractable adsorbent concept, and based on that work, the Ministry applied for a patent.

Activated carbon is known to be an effective adsorbent for removal of trace quantities of a wide range of chemicals from water. Fines generation makes both powdered activated carbon and

granulated activated carbon unsuitable for use directly in river environments.

Composite materials were prepared by melting different thermoplastic resins around granulated activated carbon. The effectiveness of these composites was poor because the carbon granules became easily separated from the plastic matrix. As well, the active surface of the carbon was reduced by the polymer coating, resulting in a reduced capacity for adsorption.

Foams, such as polyurethane, are also known to absorb trace amounts of chemicals from water, and have been used to concentrate chemicals for analysis.[2] The combination of polyurethane foam and powdered activated carbon circumvents the problems associated with encapsulated carbon granules and allows one to use the effective adsorption capacity of activated carbon and the foam in a physical form that can be applied over contaminated river bottom sediments.

Polyurethane foams containing from 30% to 39% activated carbon by weight were prepared by polymerizing the appropriate amounts of activated carbon in solutions containing polyurethane prepolymer. The resulting material was strong and had a high surface area of exposed activated carbon. The removal of tetrachloroethylene, chlorobenzene, and toluene from water using these foams was demonstrated. The foams were more effective at removing low concentrations of chemicals from water than granulated activated carbon alone, on the basis of equal mass of activated carbon. The foams produced less fines than either powdered activated carbon or granular activated carbon, when agitated in water solutions.

ABSORBENTS FOR BULK CHEMICAL SPILL CLEAN-UP

The immobilization and clean-up of bulk spills is a major concern, since this will minimise dissolution of the contaminant into the water. The major goal of Project No. 375C was to produce and evaluate a crosslinked polymer absorbent for use as an alternative river bottom clean-up method.

The use of crosslinked polymer absorbents has several advantages:
1. The volume of waste generated in the spill clean-up is greatly reduced, since the organic chemical is selectively retrieved;
2. Disturbance of the river bottom is minimal;
3. Coverage of the spill with the absorbent minimizes dissolution of the chemical into the water body itself.

Uncrosslinked and fibrous synthetic polymers, as well as crosslinked polymers, have been used for the clean-up of chemical spills on water, as they can have a high sorption capacity for organic chemicals and a low affinity for water.[3] A problem with sorbents made from both polyethylene and polypropylene fibres is that the sorbed chemical is partially released back

tweezers without disintegrating and did not turn sticky or jelly-like, it was deemed to be structurally strong.

Table 1 shows the effect of added initiator on the capacity of EVA for absorbing solvent. When less than 0.3% (w/w) initiator was used in preparing crosslinked polymer samples, the absorbent became very jelly-like upon exposure to solvent, and was easily torn apart. It was not possible to measure the absorption capacities of these samples because of their poor structural properties. At the 0.3% initiator level, the absorption capacity was found to be 49 g of tetrachloroethylene per gram of crosslinked polymer. However, the swollen polymer still lacked good mechanical strength and could not be handled easily. At levels equal to or greater than 0.4% initiator, the swollen polymer was not sticky and at levels greater than 0.4%, the swollen polymer could be handled without breaking. The absorption capacity decreased as the percentage of initiator and therefore the degree of crosslinking, increased. The measured absorption capacities ranged from 49 g solvent/g polymer for the 0.3% initiator material, to 6 g solvent/g polymer for the 6.0% initiator material.

An additional parameter that is important in the clean-up of chemical spills is the time needed to achieve maximum absorption capacity (see Table 1). For the films (0.025 in.) this time varies between one and four hours.

The optimum initiator concentration was found to be 0.5% for dicumyl peroxide. Crosslinked polymer prepared using this level of initiator picked up 30 times its weight in tetrachloroethylene after 4 hours, while maintaining good structural strength.

Table 1. MAXIMUM ABSORPTION CAPACITY & TIME TO REACH MAXIMUM ABSORPTION CAPACITY VS PERCENT INITIATOR USED IN CROSSLINKING EVA. Crosslinking was carried out by pressing at 165°C for 2 h with dicumyl peroxide as initiator. Sample thickness was 0.025 inches.

INITIATOR (%)	ABSORPTION CAPACITY (g tetrachlorethylene/ g polymer)	TIME TO REACH ABSORPTION CAPACITY (h)	DESCRIPTION
0	-	-	Dissolved
0.3	49	24	Broke
0.4	35	4	Stable
0.5	30	4	Stable &
1	17	4	stiff
2	10.6	2	enough
4	6.8	1	for
6	6	1	lifting

EVALUATION OF CROSSLINKED EVA FOR UNDERWATER SPILL CLEAN-UP

Besides absorption capacity, there are several other parameters that are of importance with respect to chemical spill clean-up. These include the desorption of chemicals from the swollen polymer, recycling of the polymer, and range of chemicals that can be absorbed efficiently.

Desorption from swollen polymer to water

The immobilization and clean-up of the bulk spill is a priority in order to minimize dissolution of the contaminant into the water. The release rate of tetrachloroethylene into water from the swollen polymer was compared to the dissolution of a pool of tetrachloroethylene into water. Crosslinked absorbent, fully swollen in tetrachloroethylene, was placed in distilled water and shaken. As a control, the same amount of solvent was placed in distilled water and shaken. The water samples were analysed by gas chromatography for dissolved tetrachloroethylene in water as a function of time. It was found that although some solvent desorbed into the water from the swollen crosslinked absorbent, the dissolution rate was 40% to 60% less than that from the pool of solvent. It was also found that only 0.4% of the solvent absorbed by the beads over a four hour period was desorbed.

Recycling of the polymer absorbent

The crosslinked EVA beads have been reused in 9 cycles of swelling in tetrachloroethylene and drying, without loss of absorption capacity or structural integrity. For application in the clean-up of bulk spills of tetrachloroethylene or other volatile solvents, a system for collecting and recycling the solvent could be devised. Once the chemical has been removed from the absorbent, it can be reused.

Demonstration of range of chemical absorption

The crosslinked EVA was examined for absorption of commonly spilled chlorinated and other organic chemicals. Table 2 shows that the chlorinated solvents were taken up in larger quantities than other organic chemicals. This is to be expected, since EVA has a high affinity for chlorinated hydrocarbons. As illustrated in Table 2, other chemicals are also absorbed to varying degrees.

The lower absorption capacities observed in the beads as compared to the crosslinked EVA films, may be due to the higher molecular weight, as well as the lower vinyl acetate content of the EVA base resin.

Table 2. ABSORPTION CAPACITY OF CROSSLINKED EVA BEADS. The polymer was crosslinked using the low temperature method with 0.5% initiator (lauroyl peroxide).

Chemical	Absorption Capacity (g chemical/g polymer)	
	2 h	92 h
Trichloroethylene	16.0	39.7
Tetrachloroethylene	8.9	17.1
Trichloroethane	6.0	11.4
Dichloromethane	6.5	8.0
Trichlorobenzene	3.8	13.1
Toluene	5.1	7.5
Xylene	4.8	7.5
Benzene	4.7	6.3
Gasoline	2.5	3.5
Hexane	0.7	2.5
Methyl Ethyl Ketone	0.5	0.6

Demonstration of spill clean-up in a river bed simulation

Prior to an actual field trial, a river bed simulation was set up in a large tank. The crosslinked beads were contained in mats made from netting material and placed upstream from a sand bag blockade in the simulated river bed. A pump was utilized to give a flow rate of 30 cm/s. When tetrachloroethylene was added to the surface of the sediment, the water carried the blobs downstream to where the mats were located. Once in contact with the polymer absorbent, the solvent was absorbed by the beads. After 96 hours, the mats were removed from the river bottom, leaving no residual solvent on the sand. The beads in the mats had absorbed the solvent "spill", and no detectable solvent was released back into the water upon removal of the mats containing the swollen beads from the tank.

SUMMARY

The use of crosslinked EVA to absorb tetrachloroethylene spills from river bottoms has been described as an example of a crosslinked polymer designed for clean-up of a specific chemical spill. The absorbent material was prepared in either sheet or bead form. The EVA beads were found to have absorption capacities in the 20 g solvent/g polymer range, had good structural integrity after absorption of the spilled chemical, showed a low rate of release into the water stream and were easily placed and retrieved from simulated river beds without

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Characterization of Leachable Metals in Industrial Wastes:

A Suggested Decision Protocol

James R. Kramer, Department of Geology, McMaster University, Hamilton, Ontario L8S 4M1

Introduction

There is an urgent need to develop a comprehensive protocol for the evaluation of the toxicity of, handling, and disposal of wastes. The procedure must consider the amount of and the mobility of a pollutant in the environment; it must be able to relate the concentration to the toxicity of the pollutant; it must include clear decision steps leading to specific actions; and it must be systematic, complete and cost-effective.

At present, there are many specific tests for the evaluation of toxic materials. The problem is that most of these tests do not lead to a systematic action path, and/or they are not conclusive enough to point to a specific action. Many of the tests are time consuming and expensive. Yet in the final analysis, they do not rigorously resolve the question of how to treat a specific waste.

Correct decision making includes three aspects: a) the nature of the waste itself, with emphasis upon the binding of the potentially toxic substance in the waste; b) the environmental conditions in which the waste will be deposited and stored; and c) the potential mobility and toxicity of the waste. Normally only a few of these points are ascertained. To make a linkage to a specific handling and storage of a waste, details on the nature of the solid/liquid matrix (a) must be known; to make a linkage to toxicity (c), a thermodynamic approach is required. The environment in which the waste will be stored (b) is key to the potential mobility of the waste. Present tests on mobility do not consider specific storage environments. In general, the key environmental factors are temperature, moisture content, bacterial activity, pH, redox potential and ionic strength. All of these factors are interrelated, and in many cases, other parameters may be manipulated to deduce another process (e.g. organic C/N content at temperature and moisture content correlated to bacterial activity). The point to emphasize is that the details of a mobility test, in general, will not coincide with the environment of waste containment. Thus one must consider the possibility that the results of a mobility test may not be appropriate for a specific storage environment.

Another approach to mobility which is rarely, if ever, used is to determine the nature of the binding of the contaminant in the heterogeneous waste. Once this association is defined, one may better estimate the potential mobility of the contaminant. This estimation may be carried out by calculation using established thermodynamic or kinetic systems and by experimentation directly on the sub-system under a variety of environmental conditions. This rather elaborate approach must be used if one is truly going to understand the fate of a contaminant.

The approach presented here is a simple decision sequence. Decisions are made using the assumption of a worst case scenario, or conservative assumptions. Furthermore, it is assumed that not one test but multiple tests will be carried out on a waste which exhibits unacceptable characteristics. The logic of the procedure is if a waste is designated as hazardous, more information is needed on the ultimate disposal or containment of the waste. This implies an intimate knowledge of the nature of the contaminant and its toxicological properties in the specific waste.

The following proposal is made specifically for metal contaminants. The ideas in general can be extrapolated to organic contaminants, but not in detail.

Background and Previous Work

There is no overall convention for the assessment and disposal of wastes. Ontario (1) has developed a registration procedure for "registerable" and "hazardous" wastes. The assessment process considers specific types of wastes, specific chemical substances, and assessment of mobility by a leachate extraction procedure (LEP). The process, however, does not assess the reason for a designation (e.g. bridging chemistry and toxicology) which is important to the final handling and containment. Furthermore, in the case of metals in wastes, it relies heavily upon the LEP, which is operationally defined and does not necessarily reflect environmental factors of containment.

There has been an enormous amount of work recently on the leaching of metals in various media. For example, one may consult the preprints of the Division of Environmental Chemistry, American Chemical Society, Annual Meeting, 1989, Dallas TX. In addition, various protocols have been developed in Ontario (Code 309, leachate extraction procedure) and elsewhere. These LEPs all rely upon adding in different ways and at different forms and amounts acetic acid to

produce a solution of about pH 5. This initial concept for this procedure was developed from an assumption of a mixture of industrial and municipal wastes, wherein all of the organic portion is converted to acetic acid (presumably by fermentation processes), and the ratio of acid to waste is determined by the mixture of the two wastes. The technique has been criticized in some detail previously (**2**) as being not representative of a stable chemical system (the pH varies greatly between acid additions), not representative of wastes in general, and of ignoring effects under reducing conditions (even though the acetic acid would have been formed in a reducing condition). Other mobilization experiments have been carried out on selected wastes to compare to the acetic acid leach procedure (LEP) (**3**). These studies have considered a sequential extraction method (**4**) and a pH stat method (**2**). In all cases, the LEP gave more variable and lower results than the chemically controlled stat or sequential extraction tests. In many cases the solution chemistry was not stable after 24 hours, the length of the LEP test. Furthermore, the stat and the sequential extraction procedures gave similar results.

Correlation of thermodynamic properties to toxicity is well known in the aquatic chemistry field (**5**). The concept is that there is a competition between the inorganic (waste) binding site and the receptor (toxic effect) binding site for a specific metal. In addition, there is a direct relationship between the binding intensity of a metal-particle and its toxic effect due to metal binding (**6**). Thermodynamic properties such as the solubility product, complexation constant, adsorption coefficient relate to the strength of binding of the metal to a substrate, and, in turn, these binding constants are readily correlated to concentrations showing lethality, reproductive impairment etc to plankton and fish (**7**).

The Proposal

There are three steps in the protocol proposal. The first step is the simplest and is an initial screening by analysis of the total potential toxic metals in the bulk waste. Step 2 comprises structural and mobility assessments of those metals in excess bulk concentration (from step 1). Step 3 is a systematic, environmentally focussed analysis of the specific toxic waste, emphasizing handling and containment.

Step 1: The decision tree starts with a straight-forward multi-element screening test for bulk composition of a waste. The question is asked, "if all of a specific metal in the waste could dissolve in its most toxic form, would it constitute a contaminant of concern?" The question is answered by comparing the bulk analysis to recommended/legislated criteria and/or to ambient soil levels. The relationships between bulk concentration, code 309 action levels and soil composition are shown in table 1 for those metals listed in code 309.

Table 1. Correlation of bulk chemistry of a waste to Schedule 4 levels for a registerable and a hazardous waste. Schedule 4 concentrations of 10 and 100 times for a 50g/L sample have been assumed to determine "Potentially Registerable" and "Potentially Hazardous". Means and ranges for surface soils for the U.S. are also given for reference. Soil data from (**9**).

	Bulk Analysis		Soils	
	Potentially Registerable	Potentially Hazardous	Mean	Range
	greater than in mg/kg solid		(mg/kg)	
Arsenic	10	100	6	<1-93
Barium	200	2000	554	15-5,000
Boron	1000	10000	34	<20-300
Cadmium	1	10	0.45	1-10
Chromium	10	100	53	1-1,500
Fluoride	480	4800	200	<10-4000
Lead	10	100	16	<10-700
Mercury	0.2	2	0.08	0.01-5
Selenium	2	20	0.03	<0.1-4
Silver	10	100	not measured	
Uranium	4	40	3	<2-4

The best and most straight-forward method for multiple element analyses at low concentrations in liquids and solids is automated wave-length dispersive X-ray fluorescence analysis (XRF). Elements with atomic numbers of 9 or greater (fluorine) can be analyzed at the "ppm" level. Modern computer driven XRF units are capable of setting their own analytical requirements using "smart systems" as well. Thus "other" metals are recognized which would not be obtained by most other methods. In addition, in round-robin analyses of metals in lake sediments, XRF consistently gave the best results (**8**). The only requirement is that the sample is fine-grained and homogeneous. For a solid, crushing grinding and pressing may be required, whereas a liquid may have to be

homogenized by blending or by using a dispersant. The method is non-destructive which dramatically cuts down on analysis time and eliminates the difficulty present with all other "wet" analytical methods of incomplete dissolution.

If the results from bulk analysis exceeds the criterion for one or more metals, then step 2 is carried out for those specific metals. If the bulk analysis falls within the guidelines, the waste is not a problem.

Step 2: The second step considers a series of other tests, according to the nature, handling and containment of the waste. The selection of tests must reflect the environmental conditions of storage and not be routine standard methods:

a) If acidity is considered a key parameter, one should carry out metal mobilization tests at specific pHs using preferably a pH stat device which can determine the amount of metal released for each H-ion added. In addition, a complete acid-base titration should be performed on the waste in order to determine its buffering characteristics (**4**). The metal mobility and acid/base characteristics give a complete information dossier on the pH dependent metal release properties. Ideally the experiments will be carried out at elevated temperature (~50°C) to ensure that equilibrium or steady state conditions have been achieved.

b) Alternately, one should carry out the Tessier sequential procedure, steps I and II, (**3**). This test too should be carried out at elevated temperature. It is important to do both steps of the test, because the degree of binding of the metal is indicated by the fractions removed in each test. If a reducing environment is anticipated, step III of the Tessier extraction, or an equivalent reducing environment test, should be run.

c) The nature of the metal in the substrate needs to be ascertained and compared to the mobility data of a) and b). X-ray diffraction analysis is useful for solids with crystalline material. In inorganic wastes such as slags and metal-plating residues, the exact association of metal and substrate can be determined. This determination allows solubility calculations under a variety of environmental conditions using computer based equilibrium programs. Secondly, scanning electron microscopy and transmission electron microscopy with elemental analysis potential are most useful on very fine-grained wastes and amorphous material.

Association of metals with other media (as indicated by morphology or chemistry) can often be inferred.

All of the information obtained in part c) must be consistent with the bulk chemistry information (step 1) and the leaching chemistry (a and b).

These results may be interpreted directly (leachate tests, steps a and b), or indirectly by solubility calculation and redox stability estimations (using the presumed environmental conditions). In the case of organic rich substrate, stability-activity relationships may be estimated directly (**8**).

If the leachate tests or the calculations indicate excess metal mobility by not conforming to established guidelines/codes, then the waste must be considered potentially hazardous, and step 3 needs to be carried out for chemical-toxicological data.

Step 3: This step is carried out if results of step 2 indicate a hazardous waste. This conclusion will normally result from leachate studies, but other analysis may be more specific in some instances (e.g. the crystalline characterization by X-ray diffraction can be more specific). This step is needed to more specifically characterize the nature of the hazardous waste, in short, to tie the chemical characteristics to toxicological characteristics. The tests suggested here are estimations of toxicity from a) the nature of the metal-coordination, b) structure-activity relationships (if not already defined), and c) direct toxicity testing. The following discusses a preferred approach to toxicity testing.

As with chemical and physical analysis, there is no one general toxicity test procedure. Toxicity tests, as with leachate tests, ignore environmental parameters which may enhance the toxic effect or suppress the toxic effect by various synergistic/antagonistic responses. These are especially important for interactions of metals with binding sites (**9**). Therefore a toxicity test which considers the total ecosystem or a series of toxicity tests is required. In the former case, Dr. Arno Rosemarin uses computer controlled swimming pools (imported from Québec) to reproduce ecosystem responses to various contaminants over time and space. The scale of a swimming pool is considered adequate to emulate most processes. In these studies, specific contaminants are added, and ecosystem responses are observed against a reference system where no contaminants have been added. Although this approach has been applied to marine ecosystems, different kinds of storage systems can be studied as well.

The advantage of this system is that a specific containment scenario can be evaluated at the whole ecosystem level prior to storage. The disadvantage of the approach is that a study is expensive and takes time.

An alternate approach is to establish an Environmental Hazard Profile (EHP) from the response of a number of model toxicity tests. Thus Freitag et al (**10**) have proposed a multiple testing approach which establishes-- a) bioconcentration in algae, fish and activated sludge, reflecting aquatic effects, b) storage, distribution and excretion in rats, reflecting effects on warm-blooded animals, c) degradation and conversion in activated sludge, reflecting microbiological modification, and d) decay and mineralization photochemically to simulate abiotic effects for atmospheric exposure. The tests proposed are all relatively standard, and the approach has been used for model toxic organic compounds. It is proposed here to use the approach to assess the heterogeneous mixture of a hazardous waste. Results for model organic compounds already tested, most of which are hazardous and under control, can be compared to a specific complex hazardous waste as far as toxic potential. It is further proposed that leachate data and compound information can be correlated with the EHP index in a structure-activity model.

The important aspect of step 3 is to determine the nature of the toxic material and what kind of effect can be expected in a containment scenario. In this way, the waste can be handled properly in the sense that its fate will be understood prior to disposal. This approach should decrease greatly the concern of processing of hazardous substances in an environmental situation.

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DEVELOPMENT OF ACexpert. 3. ENCODING RULES FOR ACdiagnosis.

Martin J. Stillman[1], Mohamed Moussa and Zbigniew Gasyna

Department of Chemistry, University of Western Ontario,
London, Ontario, Canada, N6A 5B7

ACexpert is an expert system that is designed to carry out automated analysis of metals using the technique of atomic absorption spectrometry. To date, the system specifications have been determined and a number of modules designed. In this paper, we discuss progress towards encoding the chemical rules which are used in diagnosing problems that are encountered during analyses. The use of an expert system shell, KDS3, is described. KDS3 is used to generate rules from a series of "conditions" and "conclusions" provided by the expert. The total system, bearing a number of integrated modules, is described.

Metal concentration determination using the AAS technique requires the completion of several tasks, each of which utilizes extensive knowledge and expertise. The organization, operation and control of these complex tasks are ideally suited to the application of an expert system. Our objective in the development of **ACexpert** (1,2) is to produce a system that can offer "expert" assistance during the analysis of metals. We also intend that the modules developed here for atomic absorption spectrometry will become more generally usable as models in the development of expert programs to be used during analysis by other instruments. Expert system shells are powerful tools that can be used effectively to integrate the analytical chemist's knowledge of chemical methods and quality control procedures, with the instrument control program. In this paper, we discuss progress towards encoding the chemical rules which are used in diagnosing problems that are encountered during analyses using atomic absorption spectrometry, to produce a stand-alone expert system module **ACdiagnosis**. Our experience in development of other modules of **ACexpert** is also described.

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1 Address correspondence to this author

Metal Analysis using ACexpert

A model of the laboratory procedures which are required for the completion of metal analyses by the AAS technique has been translated into a hierarchy of expert systems, Figure 1. Each expert system performs a separate task and each is capable of acting independently or as a module of the full system.

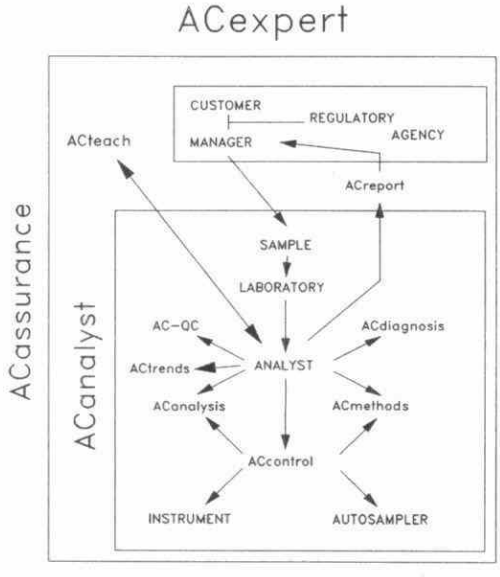

Figure 1. ACexpert: A metal analysis expert system.

Reprinted from ref. 2.

When complete, **ACexpert** will provide (i) advice on methods selection, (ii) diagnostic information for improving analytical quality, (iii) a simulation role for teaching users how to optimize their analyses, (iv) real-time control of solution preparation, sample dispensing, and sequence control, (v) control of the instrumental settings and data acquisition, and (vi) an estimation of the quality of the data obtained by the instrument. These modular expert systems are limited to a relatively narrow

domain of expertise. However, together, these modules will encompass the many varied aspects of decision-making that would be normally carried out by the human expert: from method selection, to real-time process control and then to reporting and documentation (3). Implementation of the **ACexpert** concept requires a design process that includes prototyping and validation before a production system can be completed. We have chosen to use expert system shells to aid in the development of the knowledge base (4,5), because shells contain specific strategies for knowledge representation, a complete inference engine, and a database access interface. Three of the more important types of expert systems are the consultation, interpretation, and monitoring and control expert systems. **ACmethods** and **ACdiagnosis** are consultative and interpretive types of expert system (6) while monitoring and control, and interpretation, types of expert system are combined into the analytical process control expert, **ACcontrol.** The quality control and quality assurance expert, **ACanalysis,** is based upon an interpretation type expert system. These modules are made up from four essential components: (i) a knowledge base of facts and rules, (ii) a problem solving inference engine, (iii) a knowledge acquisition module, and (iv) an explanatory interface (7). The inference engine of the expert system shell is used to allow rules and logic to be applied to facts in the knowledge base.

ACexpert has been developed using the expert system development shell KDS3 (KDS Corporation, 934 Hunter Rd., Wilmette, Il, USA). KDS3 is an inductive shell that requires that the developer specify expert knowledge in terms of examples of conditions and conclusions. The development system uses an algorithm to convert the examples into rules and to determine the order that the system will follow when questioning the user and making a recommendation. KDS3 deals with conditions, which are input into the shell as text strings that are either true, false, or known with some degree of certainty. Expert systems developed with KDS3 are set up by the developer in much the same way that they are used. The developer is prompted with questions about analysis conditions, until a conclusion is reached. In this part of the development of the expert system, the KDS3 shell is used to construct and test the rules and facts that will become part of the system knowledge base. Once completed, each KDS3 module can be used as a stand-alone expert system, as well as part of a larger system.

ACdiagnosis

ACdiagnosis is an interpretive module of **ACexpert. ACdiagnosis** is intended to solve both instrumental and chemical problems encountered with flame atomic absorption spectrometry analysis. The first versions of this program were developed using KDS3+ linked to Quick Basic (Microsoft) 4.5 routines for graphical displays. The instrumentation diagnostic section solves problems associated with factors such as solution transport (influenced by factors such as high viscosity), condition of the

burner, or flame temperature, by interrogating the user about the quality of the analytical result. From the conditions and cases describing the operation of the AAS instrument itself, the KDS3 inference engine generated 92 rules. The second section deals with chemical interference. Addition of these conditions and case conclusions increased the rule base to 248.

The 27 conditions that represent the conditions of the system are introduced and set up as statements. These statements are as follows:

1. The calibration curve is sigmoidal.
2. You are analyzing for a readily-ionizable element.
3. Low sensitivity.
4. You are using a nitrous oxide-acetylene flame.
5. You are using an oxidizing flame.
6. Signals for the same sample are inconsistent.
7. The calibration curve levels off at high concentrations.
8. The slit width is correctly set.
9. The absorption signal is abnormally noisy.
10. The monochromator is correctly set.
11. The blank value drifts.
12. The signal is increasing or decaying.
13. The signal has a slow rise time.
14. The signal value pulsates.
15. The absorption sensitivity changes.
16. The fuel pressure is low.
17. Abnormal noise at 0.00 absorption with no flame.
18. Abnormal noise at 0.00 absorption with the flame lit.
19. Occasional pulses in the absorption signal.
20. There are bubbles in the aspiration capillary.
21. The sample solutions are viscous.
22. The signal integration time is less than 1 second.
23. A refractory element is present.
24. The spectrometer is in the single beam mode.
25. The hollow cathode lamp will not strike.
26. The hollow cathode lamp will strike, but no signal is obtained.
27. The burner is above 8 on the vernier scale.

The user intervention is requested to assign "True", "False", or "Don't Know" state to each statement. These conditions, and their associated case-conclusions, are processed through the inference engine in the KDS3 shell. The rules are set up in a matrix so that the least number of answers supplied by the user, will lead to a conclusion. In the following example, the "Low Sensitivity" question is critical in

separating out the various instrumental problems that may be solved by the module. To lead to a conclusion that the glass bead is not adjusted, the user and the module logic go through a rule-based path. We should note that because of the structure of the rule base, answers to other questions were implied.

1. Statement: Low Sensitivity.
   Response: True

   Explanation: This is when you are unable to detect a weak signal normally observed with a sample.

2. Statement: Signal Increasing or Decaying.
   Response: False

   Explanation: Fluctuations of the signal during aspiration period, but not necessarily rapidly or randomly.

3. Statement: Abnormal noise at 0.0 absorption with the flame lit.
   Response: True

   Explanation: An abnormally large noise without the sample being aspirated into the flame.

4. Statement: You are using a nitrous oxide-acetylene flame.
   Response: False

   Explanation: The hotter nitrous oxide-acetylene flame could be a source of a problem.

   Conclusion: The glass bead is not correctly adjusted. The module also suggests a remedy: reset the glass bead about 1 mm from the front of the nebulizer. Set for maximum sensitivity.

The standard screen interface provided by the KDS3 shell is depicted in Figure 2. The problem at hand is displayed in the right-hand panel together with a further description of the condition, or additional information for the user.

Let us consider the generation of rules concerning the calibration curve. The first condition that is entered is "The calibration curve is sigmoidal", and the respective case conclusion for this being TRUE could be "Ionization is occurring". If False, one conclusion could be: "There is no fault". KDS3 then generates the following rules: "If the calibration curve is sigmoidal is TRUE, THEN Ionization is occurring" and "If the calibration curve is sigmoidal is FALSE, THEN Ionization occurring is FALSE". While the generation of these rules is straightforward, because KDS3 is an inductive shell, it attempts to relate all subsequent conditions to this calibration condition. The next

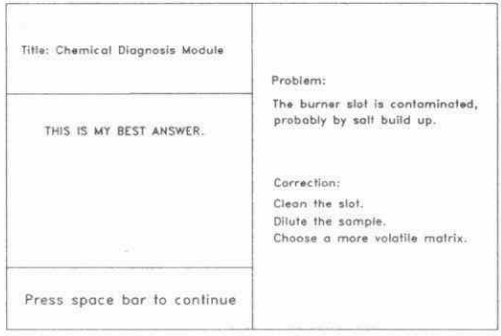
Title: Chemical Diagnosis Module
THIS IS MY BEST ANSWER.
Press space bar to continue
Problem:
The burner slot is contaminated, probably by salt build up.
Correction:
Clean the slot.
Dilute the sample.
Choose a more volatile matrix.

Figure 2. ACdiagnosis: conclusion.

condition to be entered may be "The signal is noisy". Because a noisy signal does not imply a sigmoidal calibration curve, after the appropriate case-conclusions have been entered, the development module will check the relationship of this condition to others already existing in the knowledge base. In this example, a rule will be generated "If the calibration curve is sigmoidal, THEN The abnormaly noisy absorption signal is FALSE". The logic of this rule is implied and therefore, during operation of this module, only if the answer to the sigmoidal condition is TRUE will the abnormaly noisy absorption signal condition be asked. However, generation of this type of rule can lead to problems. During development it is acceptable to respond to the questions linking conditions with "?", to imply, "There is no relationship between these conditions". Analysis of the rules generated from the condition and case-conclusions is an important step in checking the chemical logic used in this type of expert system. The best method of analyzing the logic is to analyze the truth table that links conditions and case-conclusions. We show in Figure 3, the truth table for 7 of the 27 conditions and 8 case-conclusions used in the prototype stage of **ACdiagnosis.** In this table, "T", "F" and "?" indicate the relationship between the conditions and cases.

Discussion

We have described in this paper the design and first stages in development of the expert system module **ACdiagnosis**, which is an interpretive type of expert system. While our project is centered on metal analysis, the concepts described here, are applicable to other instrumental analyses. Parallel research involves encoding expert

Conclusion	Condition: sigmoidal curve	low sensitivity	inconsistent signals	curve levels off	noisy signal	bubbles in capillary	refractory element
1 ionization	T	T	T	F	F	F	F
2 self-reversal	F	F	T	T	T	F	F
3 contamination	F	T	T	F	T	?	F
4 viscous samples	F	T	T	T	F	F	?
5 slit too large	F	T	F	T	T	F	F
6 check lamp	F	F	F	F	T	?	?
7 integration time	F	T	F	F	T	F	F
8 no problem	F	F	F	F	F	F	F

Figure 3. Part of the conditions (top) and case-conclusions (1-8) used in the ACdiagnosis module.

knowledge about the methods to be used for the analysis. We find that organizing the chemical knowledge becomes a more difficult task than writing the linking code. The KDS expert system shell has been found to fulfill our requirements for the module prototyping. The inductive logic of the knowledge acquisition engine is an important feature as it results in early validation of the instrumental and chemical rules generated. The rigorous logic that the developer follows in the KDS3 shell, results in a system that is easy to manipulate both by the developer and the user. The incorporation of the expert knowledge into an inductive shell like KDS3, in which the knowledge base is built up through step by step example-driven programming, provides a method for resolving the ambiguity of unclear rationalizations. An interfacing capability of KDS allows several modules to be linked together, as well as the capability of linking to external programs. This is essential in an expert system in which information must be transfered between a variety of modules.

Acknowledgements

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D11

Recent Advances in the Determination of Hydride-Forming Elements

Ian D. Brindle and Xiao-chun Le
Chemistry Department, Brock University,
St. Catharines, Ontario, Canada L2S 3A1

Abstract

Emission enhancement by easily ionized elements (EIEs) in direct current plasma atomic emission spectrometry has been applied to advantage by improving the signal-to-background ratio in the determination of arsenic, antimony, germanium, tin, and lead by hydride generation d.c. plasma atomic emission spectrometry. Signals of the elements were significantly enhanced with all the alkali elements and most alkaline earth elements. The alkali elements are preferred to the alkaline earth elements in improving sensitivity and detection limits because the latter gave elevated background signals. With appropriate EIE, 40-115% signal enhancement was achieved. Linear calibration and good reproducibility were also obtained with EIEs.

(Verbal presentation)

Interference effects and methods for the reduction of interferences in the determination of germanium have been studied. Simultaneous signal enhancement and interference reduction have been achieved using L-cystine, L-cysteine,penicillamine and thioglycerol. A number of amino acids, such as glycine, alanine, etc. show some capacity top reduce interferences, but this was both different from, and inferior to the reagents mentioned above. Histidine, on the other hand, proved to be superior to L-cysteinr in its ability to reduce interferences from high levels of nickel. Mechanisms are proposed to explain interference reduction and signal enhancement by thiol-containing compounds, and to explain the behaviour of amino acids as interference reducing agents.

Introduction

Signal enhancement by easily ionized elements (EIE) in direct current plasma atomic emission spectroscopy (DCP-AES) has been encountered for over two decades (1-11). In the presence of easily ionized elements, such as alkali elements and alkaline earth elements, analytical signals of other elements are usually increased. Although emission line to background ratios are often improved as well, this enhancement effect has been generally regarded as nuisance (2, 3, 12-21) due to its unpredictability. For DCP-AES determinations, variable EIE concentrations in different sample matrices make the accurate determination difficult. Even for fixed EIE concentrations, emission line enhancements differ between wavelengths of the same element, and between different elements (1, 22).

Hydride generation has been shown an efficient sample introduction technique for trace analysis (23-25). Through this process, an analyte is simultaneously concentrated as its hydride and separated from the sample matrix. Therefore, sensitivity and detection limit are improved and spectral interference is reduced. If the hydride is introduced to the d.c. plasma while an solution of EIE with constant concentration is separately nebulized and transported to the plasma jet, it should be possible to obtain an improved signal-to-background ratio which is beneficial to trace analysis. Hydride generation coupled with d.c. plasma is an ideal situation where interference by EIE could become an advantage by increasing the sensitivities and improving the detection limits of hydride-forming elements. With our previous modification of the D.C. plasma sample tube for hydride introduction (26), the experiment based on this idea is easily performed. Previous studies (25, 27) showed that with conventional aspiration and nebulization of distilled water through the outer tube into the plasma while the hydride was introduced through the inner tube, the D.C. plasma was more stable and better base line was achieved although the sensitivity remained unchanged.

The replacement of distilled water by solutions of EIEs, it was felt, could allow the signal enhancement effect of EIEs to advantage. Thus we report a series of investigations on the analysis of antimony, arsenic,

germanium, lead, and tin by hydride generation coupled with direct current plasma atomic emission spectrometry.

Hydride Generation Procedures and Parameters

A gas flowing batch system was used for hydride generation. Argon was allowed to flow continuously through the reaction vessel of the hydride generator during the entire working time. The analyte solutions were added, followed by sodium tetrahydroborate(III) solution except for the antimony determination where $NaBH_4$ was added prior to the antimony analyte solution. Because argon was kept flowing through the reaction vessel while the analyte solution and $NaBH_4$ were added, argon stripped the hydrides and then carried to the plasma. Atomic emission signals were then obtained by the echelle spectrometer. After the determination was completed, the reduced solution was drained from the reaction vessel to waste. The reaction vessel was washed three times with deionized water before the next determination was performed.

Conditions for the determination of the various elements are are given in Table 1.

Arsenic: Although previous work on arsenic determination (28) was satisfactory, especially in reducing interferences, the method required high acid concentration (5 M HCl) and 30 seconds of reaction time. In order to speed the determination, a gas flowing batch system (25) was adopted. Preliminary results showed that as the HNO_3 concentration increases from 0.01 to 0.20 M, the peak height of arsenic signals increase. High acid concentration may cause a distortion of plasma due to the large amounts of hydrogen produced. A nitric acid concentration of 0.10 M was chosen, where sufficient arsenic signal was obtained. Further, addition of L-cysteine to give a concentration of 1.0% (m/v) in the arsenic solution was found to speed the reaction and reduce interference. Therefore, 0.10 M HNO_3 and 1% L-cysteine were used to prepare both arsenic(III) and arsenic(V) testing solutions.

Antimony: A gas flowing batch system was also used for antimony determination. With the study of acid concentration on antimony determination by hydride generation, the highest antimony signal was

obtained at 0.050 M HNO_3 . Therefore, 0.050 M nitric acid was used for the preparation of antimony solution. It should be noted that even a very little $NaBH_4$ adsorbed on the reaction vessel left from previous determination can reduce antimony to its hydride. In order to avoid the uncertainty caused by unreacted $NaBH_4$, a reversed order for injection of sample and sodium borohydride solutions was used, i.e., injection of sodium borohydride prior to the sample solution to ensure that an excess of $NaBH_4$ was available. The antimony signal was observed immediately after the antimony solution was injected.

Lead: The conditions for lead determination by hydride generation has been found very critical (29). Three reaction media, $(NH_4)_2S_2O_8$ - HNO_3, H_2O_2 - HCl, and $K_2Cr_2O_7$ - malic acid, were tried for lead determination. Although $(NH_4)_2S_2O_8$ - HNO_3 system gave the highest lead sensitivity, it was more prone to interference from foreign ions, especially transition metal ions (29). It is found that with $K_2Cr_2O_7$ - malic acid as the hydride formation medium for lead, the least interference was observed. Preliminary experiments showed that 0.3% (m/v) potassium dichromate - 0.060 M malic acid, and 10.0% (m/v) sodium borohydride were the optimum concentrations for lead determination.

Results and Discussion

Enhancement of Analyte Signal and Changes of Background

Signal enhancement by EIEs is an important feature in DCP-AES. It depends on different EIEs (15, 31), concentration of EIE compounds (7, 18-20), and different elements determined (15, 30, 32). With the concern for these factors, this effect was studied by introducing each of the alkali and alkaline earth element containing solutions with various concentrations in the determination of As, Sb, Ge, Sn and Pb by hydride generation DCP-AES. Distilled water, alkali, and alkaline earth element-containing solutions, with concentration ranging from 0.10M to 2.0M, were introduced to the D.C. plasma through a conventional peristaltic pump and a pneumatic nebulizer while hydride, carried by argon, was introduced through the inner tube to the D.C. plasma. Atomic emission spectroscopic signals were then obtained with the spectrometer and recorded with a chart recorder.

Comparing the peak heights of the emission signals obtained in the presence of EIE solutions to those in the presence of distilled water, signal enhancement data and background results were calculated and shown in Table 2. The background increase(+) and reduction(-) values indicate the background changes in the presence of EIEs compared to the background in the presence of distilled water, where the latter was between 300 to 600, depending on the elements determined and the PMT and gain settings used, while the full scale of recording was 10,000 arbitrary units. The concentrations of As, Sb, Ge, Sn, and Pb solution used in performing this experiment were 20.0 ppb, 20.0 ppb, 2.0 ppb, 2.0 ppb, and 20.0 ppb, respectively.

As shown in Table 2, in all cases the As, Sb, Ge, Sn, and Pb, analytical signals were significantly enhanced with any of alkali element-containing compounds. Comparing the results obtained with aspiration of LiCl, LiOH and Li_2SO_4, and $MgCl_2$ with $MgSO_4$, we can see that the signal enhancement effect is essentially independent of anion, but depends on the cation. With the increase of alkali metal concentration from 0.10 M to 2.0 M, the signal enhancement factor increases. Although higher concentration of alkali elements may give higher signal enhancement factor, a concentration of EIE of 1.0 M is recommended since higher salt concentration may cause solid salt appear on the top of the sample tube. It is worthy of note that although the background level was changed with the introduction of alkali elements, no significant change of noise was observed.

With aspiration of alkaline earth element containing solution to the d.c. plasma as EIE source, the signal and background results are more complicated and depend on the different analytes. As we can see in table 2, in arsenic determinations, signals were enhanced and the background was decreased with any of alkaline earth elements, whereas the opposite phenomenon was observed in the case of tin determinations. In the determination of antimony and germanium, both signal and background were increased with increasing alkaline earth element concentration. For the determination of lead, Be, Ca, Sr, and Ba enhanced lead signal, whereas Mg suppressed the lead signal.

As a result of enhanced intensities of emission lines (1, 31), both peak height and peak area of emission signals were increased. There is no change in the peak width, however.

It is also found that the enhancement effect of EIE does not depend on the hydride generation procedure. As a trial, arsenic(III) and arsenic(V) were used as standards and they were made in solution with and without L-cysteine. The effect of EIEs on arsenic signals was then studied with the above reaction solutions. The results showed that same signal enhancement was observed by using either As(III) or As(V) as reaction solution. Also, similar enhancement effects were obtained in the presence and absence of L-cysteine, although L-cysteine speeded the hydride reaction and reduced the interference in the hydride generation process.

Stability of the Enhanced Signals

In conventional DCP-AES, the uncertainty and nonreproducibility caused by EIEs is a severe problem due to variable unknown EIE concentrations in different samples and to the difficulty in matching the matrix of sample and standard solutions. However, this problem is overcome in the hydride generation d.c. plasma system since the hydrides were separated from the sample matrix. Thus alkali or alkaline earth elements were not introduced to the plasma from the hydride generator along with hydride even though they were present in the sample.

Since separate introduction of EIE solutions through the peristaltic pump and pneumatic nebulizer can be easily controlled, the concentration of EIE in the plasma is kept constant. Reproducible germanium signals were obtained in with and without EIE. Eleven replicate determinations of 0.50 ppb germanium gave relative standard deviation (RSD) of 4.7% for introduction of distilled water and 4.1% for introduction of 1.0 M KCl. Similar results were obtained for lead determination, where eleven replicate determinations of 2.0 ppb lead gave RSD of 6.0% in absence of EIE and 4.6% in the presence of 1.0 M CsCl.

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Table 1. Experimental parameters for hydride generation

Element	Wavelength (nm)	Carrier Gas Flow Rate ($L\ min.^{-1}$)	Amount of Analyte	Analyte Medium	Amount of $NaBH_4$
As	193.696	0.97	5 ml 20.0 ppb	0.1 M $HN0_3$ or 0.1 M $HN0_3$ & 1% L-cysteine	1.5 ml 6%
Sb	259.805	0.97	5 ml 20.0 ppb	0.05M $HN0_3$	1.0 ml 6%
Ge	303.906	0.74	9 ml 2.0 ppb	0.015M HNO_3 & 0.4% L-Cysteine	1.5 ml 6%
Sn	283.999	1.21	5 ml 2.0 ppb	0.05M HNO_3 + 0.4g solid L-Cystine	1.5 ml 6%
Pb	283.306	0.93	5 ml 20.0 ppb	0.3% $K_2Cr_20_7$ & 0.06 M malic acid	1.5 ml 10%

Table 2. Effect of EIEs on signal and background in the determination of As,Sb, Ge, Sn and Pb *

EIE Compound	EIE Conc. (M)	Signal Enhancement (%)					Background increase (+) or reduction (-) based on a background signal of 300 -- 600 (%)				
		As	Sb	Ge	Sn	Pb	As	Sb	Ge	Sn	Pb
LiCl	1.0	24	46	-	-	60	-19	-27	-	-	n.d.
	2.0	24	44	-	-	70	-20	-25	-	-	n.d.
LiOH	0.10	-	-	5	28	26	-	-	n.d.	+7	n.d.
	0.50	-	-	13	38	56	-	-	n.d.	+14	n.d.
	1.0	-	-	15	57	60	-	-	+6	+16	n.d.
	2.0	-	-	22	61	70	-	-	+16	+18	n.d.
Li_2SO_4	0.10	5	29	5	24	37	n.d.	n.d.	-	n.d.	-
	0.50	12	39	15	41	54	-10	n.d.	n.d.	+6	-
	1.0	21	42	20	45	61	-14	-6	-	+8	n.d.
	2.0	29	66	23	55	73	-17	-11	+10	+11	n.d.
NaCl	0.10	12	17	23	39	40	n.d.	+22	n.d.	+8	n.d.
	0.50	19	24	44	52	50	-12	+9	-	+16	n.d.
	1.0	21	46	44	65	60	-19	n.d.	-	+16	n.d.
	2.0	31	61	56	83	65	-18	-21	n.d.	+19	n.d.
KCl	0.10	5	12	40	28	30	n.d.	+36	-	+8	n.d.
	0.50	21	63	57	52	50	-19	n.d.	n.d.	+16	n.d.
	1.0	26	61	78	66	70	-26	-21	n.d.	+16	n.d.
	2.0	19	3	103	76	88	-26	-41	n.d.	+21	-6
RbCl	0.50	21	51	-	-	-	-18	+21	-	-	-
	1.0	36	61	56	46	90	-30	-20	+6	+31	+7
	2.0	36	10	103	68	90	-30	-31	+10	+63	-10
CsCl	0.50	31	39	64	-	85	-33	-37	n.d.	-	-10
	1.0	41	76	-	-	90	-34	-34	-	-	-14
	2.0	19	15	-	-	115	-33	-42	-	-	-18

EIE Compound	EIE Conc. (M)	Signal Enhancement (%)					Background increase (+) or reduction (-) based on a background signal of 300 -- 600(%)				
		As	Sb	Ge	Sn	Pb	As	Sb	Ge	Sn	Pb
$BeSO_4$	1.0	12	37	18	-25	14	n.d.	+71	+330	+86	+71
	2.0	-	-	24	-46	14	-	-	+450	+130	+100
$MgSO_4$	1.0	26	66	49	-100	-59	n.d.	+78	+150	+1400	+1500
	2.0	36	66	57	-	-	-6	+59	+260	-	-
$MgCl_2$	1.0	29	68	-	-	-69	n.d.	+70	-	-	+1500
	2.0	36	76	-	-	-	n.d.	+73	-	-	-
$CaCl_2$	1.0	38	56	43	-55	73	-10	+60	+110	+270	+140
	2.0	36	63	54	-	73	-11	+77	+360	-	+250
$SrCl_2$	1.0	38	42	49	-25	95	n.d.	+74	+130	+180	+130
	2.0	-	-	49	-55	73	-	-	+450	+300	+220
$BaCl_2$	0.50	19	37	29	0	77	-7	+110	+320	+150	+200
	1.0	19	39	43	-26	50	-9	+110	+580	+290	+340

*: "n.d." -- The change is not detectable.
"-" -- not determined.

D13

APPLICATIONS OF GC/MS/MS FOR THE ULTRA-TRACE DETERMINATION OF CHLORINATED DIBENZO-p-DIOXINS AND DIBENZOFURANS IN COMPLEX ENVIRONMENTAL SAMPLES

E.J. REINER, D.H. SCHELLENBERG, V.Y. TAGUCHI,
D.M. McCURVIN AND R.E. CLEMENT
ONTARIO MINISTRY OF THE ENVIRONMENT
REXDALE, ONTARIO, M9W 5L1, CANADA

The analysis of chlorinated dibenzo-p-dioxins (CDD) and dibenzofurans (CDF) in complex matrices, which oftentimes contain chemical interferences at concentrations several orders of magnitude greater than those of the CDD and CDF, requires extensive sample cleanup prior to instrumental analysis. Limitations in sample cleanup place additional demands on the instrumentation.

The difficulties in the analysis of environmental samples make selectivity and sensitivity important considerations for the method of choice. Capillary column high resolution gas chromatography / high resolution mass spectrometry (HRGC/HRMS) has been the standard method for analyzing CDD and CDF in complex matrices such as sediments, effluents and biological tissues.

Single reaction monitoring (SRM) on tandem mass spectrometers can also be used to achieve the enhanced selectivity and corresponding sensitivity required for the analysis of CDD and CDD in complex matrices. The signal strength of the daughter or progeny ions in SRM are strongly dependent on a number of parameters, such as: collision gas pressure, collision energy, electron energy, nature of the collision gas, the energy of Q_3 relative to Q_2, the design of the collision cell and the type of the detector. In order to maximize the signal strength of the progeny ions, these parameters must be optimized.

Until recently, tandem mass spectrometry (MS/MS) has been able to meet the requirements for selectivity but has been approximately one order of magnitude less sensitive than HRGC/HRMS methods. Optimization of tuning parameters using 1 ug of the analyte of interest in a direct insertion probe (DIP) [1] rather than PFTBA resulted in sensitivities comparable to the HRGC/HRMS technique reported previously [2]. Table 1: compares the limits of detection, reported in 1986, by three manufacturers of triple quadrupole mass spectrometers, using PFTBA or PFK for tuning, to the limits of detection that were obtained when dioxins and furans were used for tuning and to limits of detection obtained by HRMS. Most of the limits of detection obtained by the MS/MS dioxin tune method are between one and two orders of magnitude lower than when PFTBA or PFK is used for tuning and almost as low as those obtained by HRMS.

Collision induced dissociation breakdown graphs were used initially to optimize parameters such as collision energy and

collision gas pressure. The breakdown graphs for PFTBA, 2,3,7,8-Cl_4DD and 2,3,7,8-Cl_4DF plotted vs. collision gas pressure are shown in Figure 1. The optimum collision gas pressure for the dioxin and furan was 3.3 mtorr while that for PFTBA was 0.7 mtorr. Figure 2: shows the breakdown graphs of PFTBA and four Cl_4DD congeners. The optimum collision energy for PFTBA was 25 eV while those for the dioxins were between 20 and 28 eV. The variation in optimum collision energy for the four Cl_4DD congeners implies that the relative response factors within a congener group are dependent on collision energy. Figure 3: shows the mass chromatogram of a mixture of three Cl_4DD congeners (1,2,3,4-, 2,3,7,8-, and 1,2,7,8-). Injection A was run with parameters set to optimize 2,3,7,8-Cl_4DD while injection B was set to optimize 1,2,3,4-Cl_4DD. As expected, the signal strength of 2,3,7,8-Cl_4DD was enhanced in injection A and the signal strength of 1,2,3,4-Cl_4DD was enhanced in injection B. In order to obtain reproducible relative response factors, a 2,3,7,8-containing (the most toxic) congener was chosen for each group. These are shown in Table 2.

Each probe sample was prepared by evaporating 1 ug standards of a furan and the corresponding dioxin with the same number of chlorines in the same sample cup. Each of the five cups (Cl_4DF/DD to Cl_8DF/DD) was inserted in turn into the mass spectrometer using the DIP and parameters such as collision gas pressure, collision energy, electron energy, lens voltages, quad offsets, etc. were optimized for both the furan and dioxin.

Another factor that increased the signal strength of the dioxins and furans was elevation of the source temperature to 250^{o}C. This enhanced the signal strength of the congeners of higher chlorine substitution. Also, a high trap current (300 uA) and a Finnigan 4500 ion volume instead of the normal TSQ-70 ion volume was used to increase the flux of the ionizing electrons into the ion source.

The advantages obtained by using the dioxin tune method include: good sensitivity - less than 1 picogram of dioxins and furans can be detected for all congeners; infrequent tuning - about 3 to 4 times a year @ 200 injections / month with source and rod cleaning every six months (ion volumes are changed daily); and selectivity - the reduced chemical noise gives an increase in the S/N ratio and therefore an enhancement in sensitivity over single quadrupole instruments.

Example 1 shows the mass chromatogram of a 500 fg standard injected on a 30m SE-52 capillary column with a split/splitless injector. Note the signal to noise is about 10:1. Example 2 shows 2pg of 2,3,7,8-Cl_4DD in a fish extract injected on the same column using the "DOW" only cleanup. This sample was injected about 3 weeks after the last time the instrument was optimized (tuned). Example 3 shows a comparison of a fish extract (Dow only cleanup) run on both a ZAB-2F and TSQ-70 mass spectrometer. Note that the chromatogram of the sample determined by MS/MS is much cleaner than that determined by HRMS at 12,000RP. Example 4 shows the mass chromatograms of an effluent sample. Note that the relative response factors obtained in the GC/MS/MS mode, when 2,3,7,8- dioxins and furans are used for tuning, are very similar to those obtained in the GC/MS mode. This indicates that the

the total concentration determination for a congener group would be similar in both the GC/MS and GC/MS/MS modes.

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TABLE 1: MOE MS/MS COMPARISON
LIMIT OF DETECTION

CONGENER	MANUFACTURER A	B	C	PRESENT METHOD	HRMS[1]
Cl_4DD	2	2	8	0.3	0.2
Cl_5DD	5	4	9	0.5	0.2
Cl_6DD	10	10	23	0.3	0.2
Cl_7DD	15	15	19	0.3	0.2
Cl_8DD	20	25	38	0.6	0.4
Cl_4DF	4	3	7	0.3	0.2
Cl_5DF	5	4	11	0.3	0.2
Cl_6DF	10	8	21	0.2	0.2
Cl_7DF	15	10	20	0.5	0.2
Cl_8DF	20	20	19	0.5	0.2

ALL DATA IN PICOGRAMS

TABLE 2: Congeners Used for Tuning in MS / MS

2,3,7,8-Cl_4DD
1,2,3,7,8-Cl_5DD
1,2,3,4,7,8-Cl_6DD
1,2,3,4,6,7,8-Cl_7DD
Cl_8DD

2,3,7,8-Cl_4DF
1,2,3,7,8-Cl_5DF
1,2,3,4,7,8-Cl_6DF
1,2,3,4,6,7,8-Cl_7DF
Cl_8DF

FIGURE 1 : COLLISION GAS PRESSURE BREAKDOWN GRAPHS

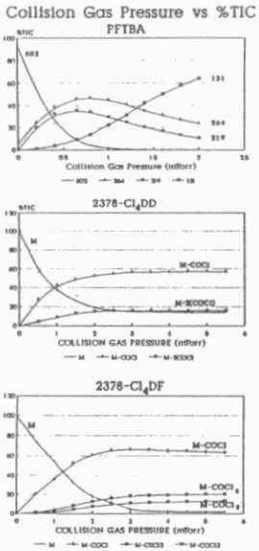


FIGURE 2 : COLLISION ENERGY BREAKDOWN GRAPHS

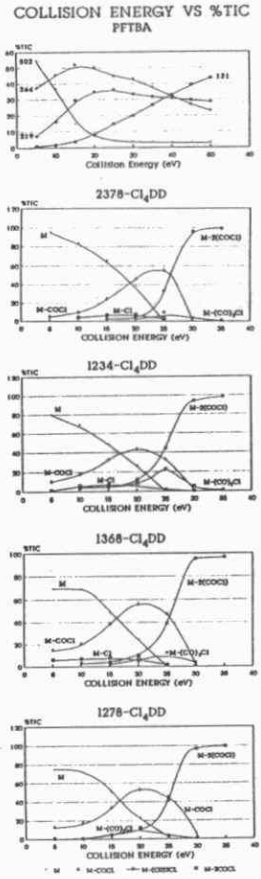
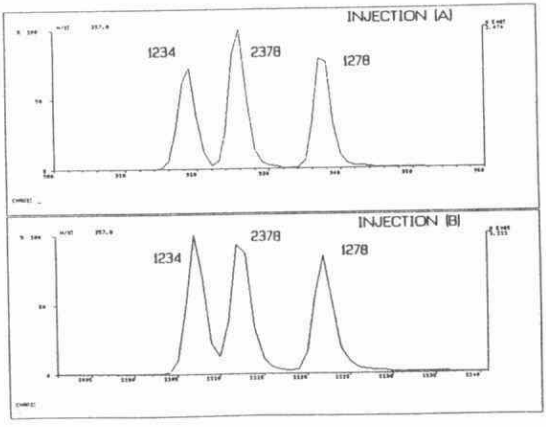
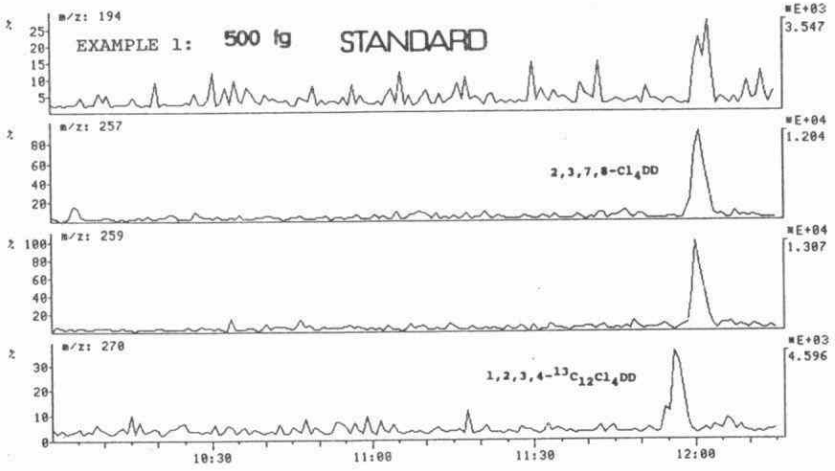
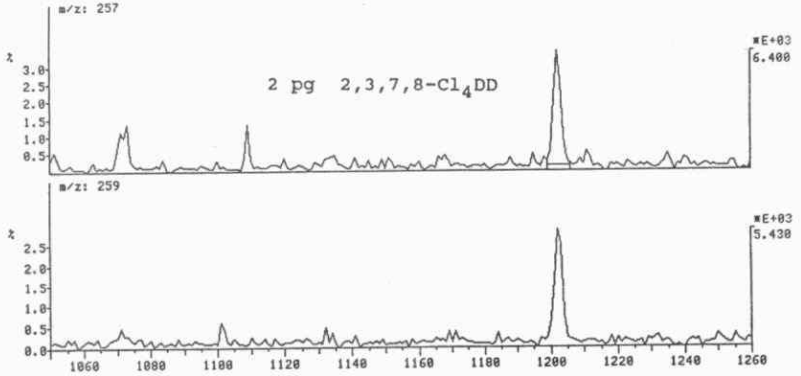


FIGURE 3: Cl_4DD STANDARDS (100pg)



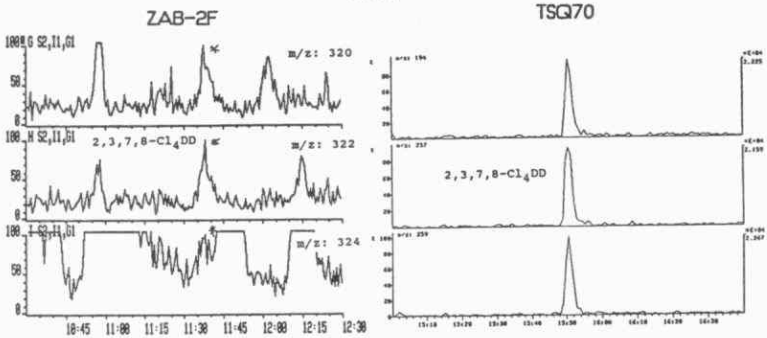


EXAMPLE 2: FISH

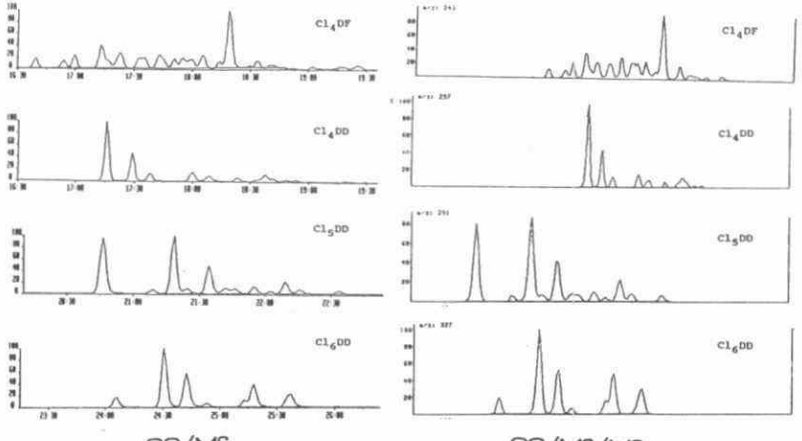


EXAMPLE 3:

FISH



EXAMPLE 4: COMPARISON OF RELATIVE RESPONSE FACTORS



D14

DEVELOPMENT OF GC CAPILLARY COLUMN FOR ANALYSES OF MOST TOXIC ISOMER OF PCDD, PCDF AND PAH IN ENVIRONMENTAL SAMPLES.

K. P. Naikwadi*, B. Ross and F. W. Karasek.
Department of Chemistry, University of Waterloo, Waterloo, Ontario, N2L 3G1.

ABSTRACT:

Analysis of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) has been performed using gas chromatography mass spectrometry (GC-MS). Analysis of the most toxic isomers, in particular, 2,3,7,8-substituted PCDD/PCDF in the presence of other isomers requires a special isomer specific capillary column or high performance liquid chromatography (HPLC) fractionation prior to GC-MS analysis. Commercially available long (>50 m) polar columns can separate 2,3,7,8-TCDD from other tetra isomers. However, those columns are not satisfactory for the analyses of total PCDD/PCDF in the environmental samples. Gas chromatography -high resolution mass spectrometry (GC-HRMS) and GC-MS/MS techniques are not helpful in the analysis of 2,3,7,8-TCDD unless it is separated from the other tetra isomers. The analysis of 2,3,7,8-TCDD and total PCDD and PCDF in a single GC-MS run can ease the laborious techniques presently used. In this study we have developed a new stationary phase for the GC capillary column. The capillary column developed using this new stationary phase showed unsurpassed selectivity for the separation of 2,3,7,8-TCDD from other tetra isomers. There are several advantages of the newly developed GC capillary column. It can be used for the analyses of total PCDD/PCDF in addition to 2,3,7,8 TCDD in all kinds of environmental samples. The most toxic 2,3,7,8-TCDD is eluted as the last isomer in all 22 tetra isomers using the new column with GC-MS. More than one minute retention time difference between 2,3,7,8-TCDD and the closest eluting 1,2,8,9-TCDD isomer guarantees no overlap even in the case of column deterioration or a very high concentration of 1,2,8,9-TCDD. Separation and quantitation results for 2,3,7,8-TCDD in various environmental samples using a column developed in this study and a commercial polar column (SP-2331) are compared. Applications of the newly developed column for the separation of other toxic isomers which are difficult to separate on conventional columns will also be discussed.

INTRODUCTION:

The analysis of environmental samples for PCDD requires rigorous methodology for positive identification and quantitation. Environmental samples give several difficulties due to sample complexity and strong interferences of other chlorinated organic compounds. GC-MS in the electron impact selected ion monitoring (EISIM) mode is generally used for analysis of PCDD. Use of open column chromatography and HPLC for sample clean up and then GC-MS analysis of PCDD in fish [1], sediments [2], fly ash [3,4] samples have been reported. Extreme care is required in sample preparation and measurement procedures in order to eliminate the possibility of false positive or false negative results due to interferences. This difficulty in PCDD analysis can be eased if samples are spiked by a C-13 labelled dioxin mixture containing all the C-13 labelled dioxin isomers[5,6]. However, the analytical methodology can be simplified if a gas chromatographic column can separate the interfering compounds as well as the isomers in all congener groups of dioxins and dibenzofurans. Based on the results of whole animal studies and in vitro assays, the symmetrically substituted 2,3,7,8-TCDD isomer appears to be the most toxic. A factor of 100 to 10,000 difference in toxicity can be found for the closely related 2,3,7,8-TCDD and 1,2,3,8-TCDD isomers[7,8]. Current techniques for the analysis of 2,3,7,8-TCDD in environmental samples are time consuming and not completely satisfactory. This paper shows the unique selectivity of a capillary column developed in our laboratory for the separation of 2,3,7,8-TCDD/TCDF from other tetra isomers. Separation of the most toxic 2,3,7,8-substituted PCDD/PCDF isomers also can be achieved on the new capillary column using GC-MS/EISIM technique.

EXPERIMENTAL:

The GC-MS system used was a Hewlett Packard 5987 with an HP 1000 data system, cool on column injector, and splitless direct interface between the GC and MS.
Fused silica capillary tubing (25 m X 0.32 mm I.D.) was coated using the static method by the newly developed liquid crystalline polysiloxane stationary phase. The column was then conditioned by heating from 40°C to 270°C at 2°C/min. The following temperature program was used for analysis of PCDD/PCDF using the new column in GC-MS.

Oven temperature	80°C for one minute
programmed to	200°C at 4°C/minute
programmed to	260°C at 2°C/minute
final time	30 minutes.

The ion source temperature was 200°C. A mixture of PCDD/PCDF synthesised in our

laboratory and individual standards of 2,3,7,8-substituted PCDD/PCDF isomers available from commercial sources were used to determine the selectivity of newly developed column. The ions monitored for the tetra- to octa-chlorinated dibenzo-p-dioxins and dibenzofurans were M, M+2, M+4 or M+2, M+4, M+6 for each congener group. The PCB mixture containing many different isomers was prepared by mixing the commercial Aroclors (1216, 1242, 1248, 1254 and 1260).

RESULTS AND DISCUSSION:

The complete separation of 2,3,7,8-TCDD from all other tetra-CDD isomers and from PCB using newly developed capillary column by GC-MS is shown in figure 1. For the positive identification and quantitation of 2,3,7,8-TCDD in complicated environmental samples such as PCB accidental fire samples, it is necessary to separate 2,3,7,8-TCDD from interfering PCB. It can be seen from figure 1 (mass chromatogram for 2,3,7,8-TCDD, trace C) that 2,3,7,8-TCDD has been completely separated from peaks produced by PCB (mass chromatogram for 321.9 ion, trace A) that can interfere in TCDD quantitation. The selectivity based on the molecular weight can be achieved using HRGC-MS/EISIM or HRGC-HRMS or HRGC-MS/MS techniques. However these techniques are not useful for the separation of 2,3,7,8-TCDD from other tetra isomers. It can be seen from figure 1 that 2,3,7,8-TCDD has been completely separated from all tetra-CDD (see figure 1, trace B, and C) isomers in the synthetic mixture. The selectivity of this new column can be explained based on the mechanism of separation on liquid crystal stationary phases. From the isomers with similar volatilities , the linear and symmetrical isomers will be retained longer than the bulkier isomers because the linear and symmetrical isomers favours the geometry of the liquid crystal stationary phase. The 2,3,7,8-TCDD is the most symmetrical and linear of all 22 TCDD isomers and hence elutes after all TCDD isomers. The separation achieved using the new column and GC-MS selected ion monitoring (SIM) technique for a synthetic mixture that contain all isomers of tetra- to octa-chlorodioxin congeners is shown in figure 2. The last peak in the mass chromatogram for TCDD was confirmed to be 2,3,7,8-TCDD. Identification of other separated isomers, in particular, 2,3,7,8-substituted PCDD using this column is shown in figure 2. Separation and identification of 2,3,7,8-substituted PCDF is under investigation. There are several advantages of the newly developed column for analysis of environmental samples. It can be used for the analysis of the total PCDD/PCDF in addition to 2,3,7,8-TCDD in all environmental samples. The most toxic 2,3,7,8-TCDD is eluted as the last isomer in all 22 TCDD isomers. More than one minute retention time difference between 2,3,7,8-TCDD and the closest eluting 1,2,8,9-TCDD isomer guarantees no overlapping in the case of minor column deterioration or a very high concentration of 1,2,8,9-TCDD.

Separation of polycyclic aromatic hydrocarbons achived using the new column is shown in figure 3. Unique selectivity for the separation of anthracene from phenanthrene and

benzo(a)pyrene from benzo(e)pyrene shows the potential of the new column for separation of structural isomers that are difficult or impossible to analyze using commercially available columns.

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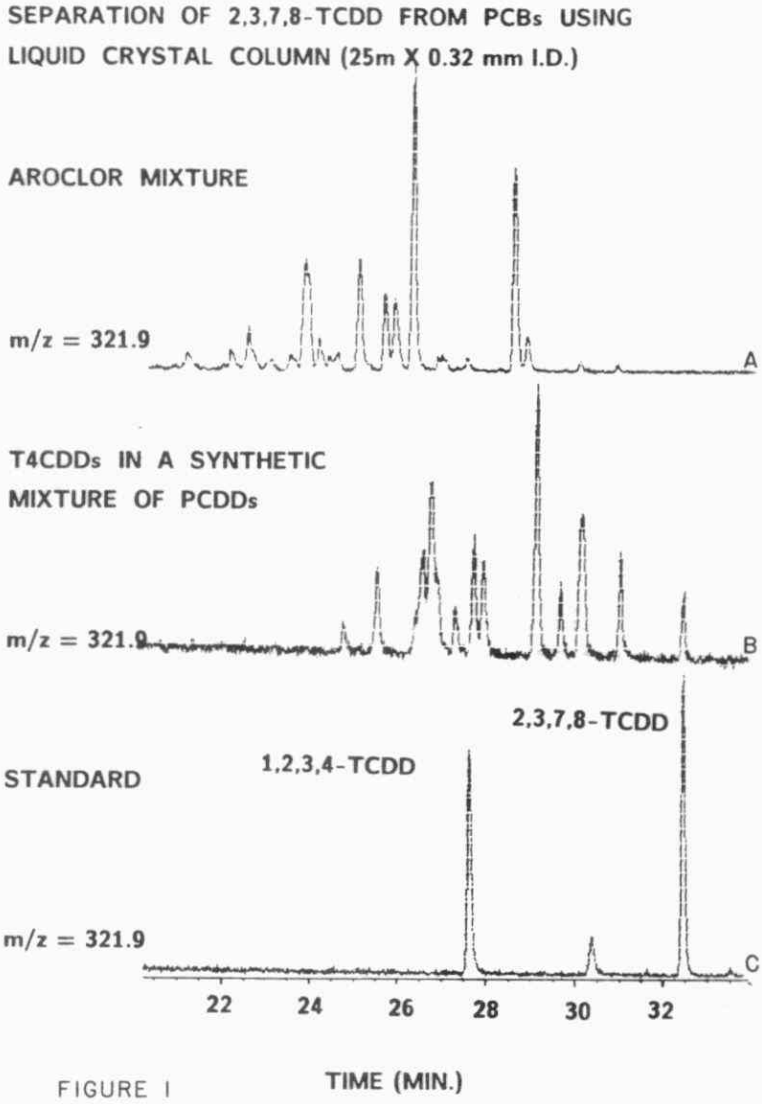

SEPARATION OF 2,3,7,8-TCDD FROM PCBs USING
LIQUID CRYSTAL COLUMN (25m X 0.32 mm I.D.)
AROCLOR MIXTURE
m/z = 321.9
A
T4CDDs IN A SYNTHETIC
MIXTURE OF PCDDs
m/z = 321.9
B
2,3,7,8-TCDD
1,2,3,4-TCDD
STANDARD
m/z = 321.9
C
22
24
26
28
30
32
TIME (MIN.)

FIGURE I

SEPARATION OF TETRA- TO OCTA- CHLORODIBENZO-p-DIOXINS SYNTHETIC MIXTURE USING LIQUID CRYSTAL FUSED SILICA CAPILLARY COLUMN, 25 m x 0.32 mm ID, BY GC-MS SYSTEM

FIGURE 2

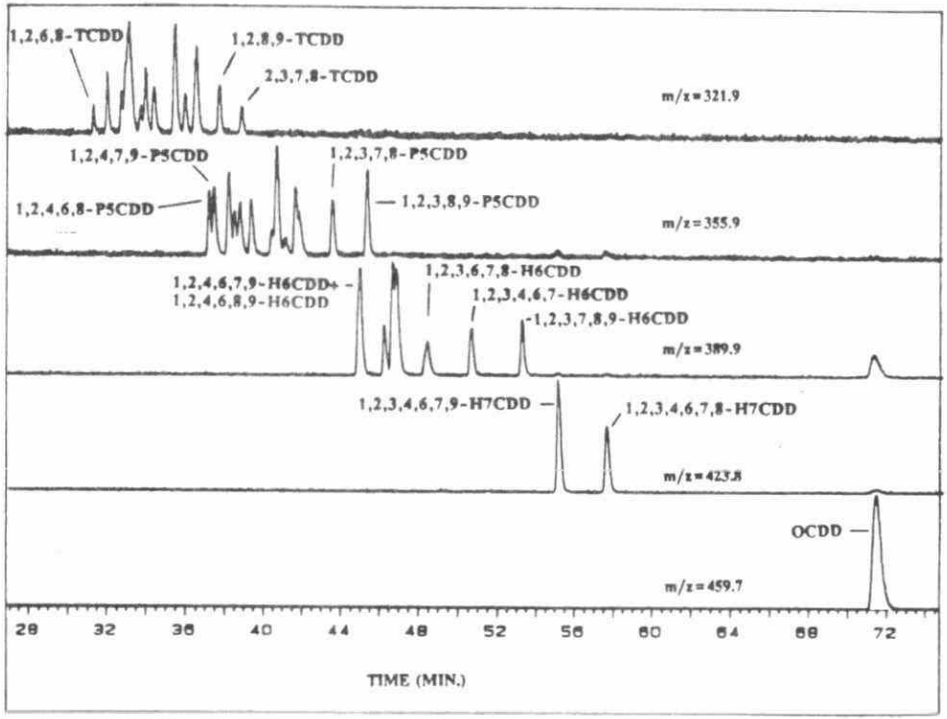
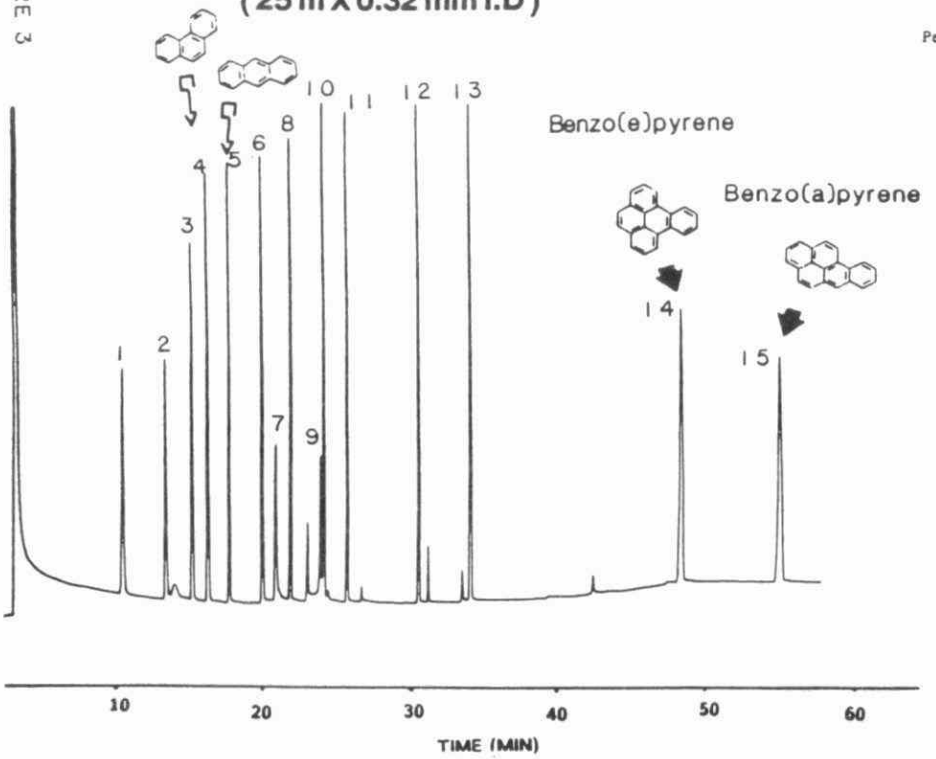


FIGURE 3

SEPARATION OF PAHs USING LIQUID CRYSTALLINE POLYSILOXANE COLUMN (25 m X 0.32 mm I.D)



Peak#	Compound
1	9H-Fluorene
2	9H-Fluorene, 1-methyl
3	Dibenzothiophene
4	Phenanthrene
5	Anthracene
6	Phenanthrene, 1-methyl
7	Anthracene, 9-methyl
8	Fluoranthene
9	Anthracene, 2-methyl
10	Pyrene
11	Anthracene, 9,10-dimethyl
12	11H-Benzo(b)fluorene
13	Triphenylene
14	Benzo(e)pyrene
15	Benzo(a)pyrene

D15

SOLID SUPPORTED ISOLATION AND DERIVATIZATION: AN APPROACH TO AUTOMATION FOR ANALYSIS OF ENVIRONMENTAL WATER.

Jack M. Rosenfeld, Y. Moharir, F. Matthew-Ahlang.

Department of Pathology
McMaster University

INTRODUCTION:

Determination of the chlorophenoxy acetic acid (CPAA's) herbicides and the corresponding breakdown products from water ie the chlorophenols (CP's) requires two major processes. Analytes must first be isolated from matrix and then derivatized at the acidic functionalities. Pentafluorobenzylation (1), silylation (2) with cyano containing reagents and esterification with methanolic BCl_3 (3) have been used to prepare the derivatives for gas chromatographic determination of parent herbicides and the corresponding phenols. Standard EPA procedures are based on derivatization with pentafluorobenzyl bromide (PFBBr) but the process is complex and involves use of toxic catalysts such as crown ethers (1). The appropriate use of solid supported processes could be used to simplify such procedures and eliminate the use of toxic materials in the analytical laboratory.

There are two distinct processes that can be exploited in sample preparation. The first is adsorption used for isolation of organics from aqueous matrix (4). The second is process is solid supported reaction. Use of in-line and off-line solid supported reactions in automated and semi-automated determination of drugs by high pressure liquid chromatography has been described and reviewed (5,6).

We investigated the use of XAD-2 solid supported reactions of CPAA's and CP's in aqueous solutions. This approach was taken to reduce the technical complexity of sample preparation and to improve the occupational safety of the analyst. Electrophoric and water insoluble pentafluorobenzyl (PFB) derivatives suitable for gas chromatography were prepared directly from buffered water by reaction of CPAA's and CP's with PFBBr supported on XAD-2 (7-12). Derivatization with Benzyl bromide (BzBr) was also investigated as a means of reducing the amount of interferences encountered with PFBBr. In conjunction with this derivatization procedure we also developed in-line chromatographic separation of derivatized analytes from each other and from interferences.

EXPERIMENTAL:

Apparatus: The derivatives of the analytes were determined on a Helwett-Packard (H-P) 5710 or 5790 gas chromatograph equipped with a pulse linearized electron capture (ECD). The 5710 instrument was equipped with a 15 m DB-1 megabore column with an inner diameter

of 0.53 mm and a film thickness of 1.5 micrometers. The 5790 instrument was equipped with a 30 m DB-1 J & W fused capillary column with an inner diameter of 0.32 mm and a film thickness 0.25 micrometers. The output of the detectors was monitored on H-P 3390A recording integrators. Hydrogen was used as a carrier gas for the megabore column the flow rate was set at 4 mL/min and for the capillary column it was set at a linear velocity of 62 cm/sec at 180 C and 10 % methane in argon was used as a make-up gas at a flow rate 15 ml/min.

Reagents: Pentafluorobenzyl bromide and BzBr were purchased from Caledon Laboratories, Georgetown, Ontario, and from Aldrich Canada respectively. The macroreticular resin, XAD-2, a cross-linked copolymer of styrene/divinylbenzene was obtained from BDH Laboratories, Toronto, Ontario and was cleaned and stored as previously described (13). Florisil, basic alumina, disposable 1 ml Supelclean columns for semi-preparative chromatography and a vacuum module were also purchased from Supelco (Canada) Oakville Ont. Solvents were purchased from the usual commercial suppliers, such as Fisher, BDH and Aldrich Canada. Pure analytes were obtained from the E.P.A Repository.

All the glassware was silylated by standard procedures. Glassware and plasticware was washed with methylene dichloride, methanol, acetonitrile and dried prior to use.

Preparation of PFB and Bz Derivatives: Derivatives of the pure analytes were prepared by stirring of the organic acid in acetone with PFBBr or BzBr with K_2CO_3 as the base. Reaction work-up consisted of evaporating the acetone, extracting the residue with CH_2Cl_2 and finally washing the organic phase with distilled water. The PFB products were purified by thin-layer chromatography.

Derivatization and Isolation: Three hundred mG of XAD-2 was added to glass 16X100 mm or 25X200 mm screw cap vials and wetted with 300 uL of acetonitrile. The smaller reaction vials were charged with 4 mL of 0.1 M Phosphate buffer at pH 7.4 and containing 5 nG/mL each of 2,4-Dichlorophenol (2,4-DiClCP) 2,4,5-Trichlorophenol (2,4,5-TriClCP) and 2,4-Dichlorophenoxy acetic acid (2,4-DiClCPAA). The larger vials were charged with 20 mL of the phosphate buffer but containing only the 2,4-DiClCPAA. For recovery studies the 4 mL or 20 mL of aqueous phase were treated with C^{14} radiolabelled 2,4-DiClCPAA.

The reaction was initiated by adding 150 uL of reagent (PFBBr or BzBr) in hexane (1/9 v/v) and the reaction mixture was shaken in a water bath for varying times at 40°C or 50°C. The resin was isolated by filtration in a 5 mL Supelclean cartridge and washed with distilled water which was removed by suction. After removal of bulk water by filtration, 100 μL of acidified 2,2-dimethoxypropane (DiMP) was added as a water scavenger and allowed to remain in contact with the resin for 15 minutes. Excess

scavenging reagent and products of hydrolysis (acetone and methanol) were removed with a slow stream of nitrogen at room temperature.

For the purification of the PFB derivatives cartridge containing the dried XAD-2 was then inserted linked in series to a 1 mL cartridge containing Florisil and a 1 mL cartridge containing basic alumina. Elutions were carried out using a Supelco Vacuum module. Derivatized phenols were eluted from the XAD-2 - Florisil - Alumina link with 30 mL (3 column volumes) hexane/ toluene (95/5 v/v). The Florisil and Alumina columns were then separated. In one experiment the 2,4-DiClDPAA PFB ester was eluted with 30 mL 25% and 30 mL 50% CH_2Cl_2 in hexane. In a second experiment the Florisil column was linked to a silica gel column and the link was washed with 30 mL 25% and 30 mL 50% CH_2Cl_2 in hexane with the analyte eluting in the latter eluent.

For isolation of 2,4-DiClCPA Bz ester the cartridge with the XAD-2 was simply linked to a column of florisil. The linked system was washed with 24 mL hexane followed by hexane/ toluene (95/5 v/v). The 2,4-DiClCPA Bz ester was eluted with 50% hexane/ CH_2Cl_2.

Gas Chromatography: Samples were analyzed by gas chromatography with electron capture using the columns described above. For the capillary column the following temperature conditions were used: 170-215°C at 4°C/min; 215°C to 300°C at 20 °C with a 2 minute hold at 300°C. For the megabore the initial temperature was 170°C, the rate of increase was 4°C and the final temperature was 290°C. There was no delay at the initial or final temperatures.

Calculation of Yield and Reaction Rate : Yield of the reaction was calculated based on the recovery of radiolabel when the reaction was carried out with C^{14} 2,4-dichlorophenoxy acetic acid. The PFB derivative, but not the parent carboxylic acid, eluted from the chromatographic systems described above; accordingly the recovered radiolabel represented the yield of the reaction for carboxylic acids. The reaction rate was calculated form the rate of disappearance of the radiolabel from aqueous solution.

RESULTS AND DISCUSSION:

Development of analytical techniques for the determination of herbicides and related compounds requires that several distinct problems be addressed. Firstly two distinct functional groups, the carboxyl and phenol are involved. Many herbicides contain the former functionality but are degraded in the environment to phenols. Secondly, numerous interferences are found in water matrix.

Derivatization of organic acids in heterogeneous aqueous/ organic systems requires that pH be 2 log units above the pKa of

the acid in order to ionize the acid. Accordingly at alkaline conditions both the phenols and 2,4 dichlorophenoxy acetic acid should be expected to react. In our hands, the PFB ester of the acid was not recovered at alkaline conditions whereas PFB ethers of 2,4-DiCP and 2,4,5-TriCP were formed and isolated. The reason for this is not clear. This is the only carboxylic acid which could not be pentafluorobenzylated under these conditions.

Simultaneous adsorption/ derivatization to PFB derivatives of all the analytes was possible at pH 7.4. Thus both parent herbicide and the degradation product could be isolated under the identical reaction conditions. Amongst all phenols studied to date in our laboratory (7,10,12,13) only the chlorinated analytes were derivatized by XAD-2 supported derivatization at pH 7.4. This reflected the lower pKa of chlorophenols, the irreversible reaction and the lipophilicity of the products.

Isolation coupled with pentafluorobenzyaltion in a single step was insufficient for developing methods of high sensitivity. The matrix of lipophilic compounds that can interfere, even when limited to ordinary laboratory reagents and water, is quite complex and is particularly "rich" in even carbon numbered organic acids of mammalian origin. Separation of derivatized analyte from such interferences was essential. Linking the XAD-2 resin reactor bed directly to the chromatographic columns proved a viable separation system; **providing that the chemical drying step with DiMP was used.**

Florisil alone was not effective at separating the PFB derivatives of the analytes from the some of the interferences since many of these compounds co-eluted with PFBBr. As a result more complex linked system consisting of an XAD-2 - Florisil - Basic Alumina followed by XAD-2 - Florisil - Silica Gel were investigated (Fig. 1). The second link was required because 2,4-DiClCPAA PFB ester could not be recovered from basic alumina which was effective at retaining the interferences to determination of PFB ethers of the phenols. Moreover, Florisil alone was not effective at completely removing interferences to determination of 2,4-DiClCPAA PFB ester. Thus after elution of the PFB-ethers the Alumina column was removed and the Florisil column linked to a Silica Gel column. Eighty to 90% of the derivatized fatty acids were eluted from the XAD-2 -Florisil - Silica Gel link with were eluted with 25% CH_2Cl_2 in hexane.

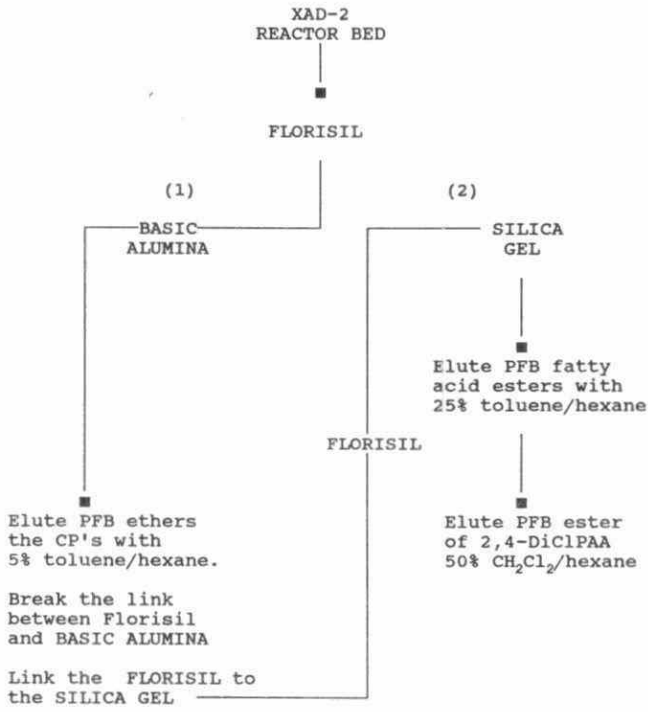


Figure 1: Schematic for semi-preparative chromatographic isolation of PFB ethers of 2,4-Dichlorophenol 2,4,5-Trichlorophenol and the PFB ester of 2,4-Dichlorophenoxy Acetic Acid

The 2,4-DiClCPAA PFB ester was eluted from the XAD-2-Florisil-Silica Gel link with 50% CH_2Cl_2 in hexane but this fraction contained the remaining portion of the fatty acid PFB esters. Recoveries for pentafluorobenzylation of 2,4-DiClPAA with PFBBr from 4 mL and at a reaction time of 2 hours was 66%. From 20 mL the yield at 4 hours was 50%.

Derivatization with BzBr was investigated in order to simplify the semi-preparative chromatographic clean up and eliminate interferences due to fatty acids. The rationale was that this reagent would not produce any electrophoric derivatives or by-

products which were found with PFBBr and which necessitated the complex chromatographic procedure. The reaction with BzBr proceeded at a somewhat slower rate. Yield for esterification of 2,4-DiClDPAA with BzBr from 20 mL was 30% in a 4 hour reaction time and 50% in 24 hours. The purification of the 2,4-DiClDPAA Bz ester was markedly simplified and semi-preparative chromatography on a single column was sufficient to produce an isolate that contained only the derivative and interferences due only to endogenously electrophoric materials in solvents, glassware and plasticware (16). These compounds were found in the sample, the blank containing BzBr, in the blank that contained no reagent and two compounds were found in residues of evaporated hexane and CH_2Cl_2 (Fig. 2). Future work will reduce these interferences by being carried out in glass cartridges.

It proved difficult to improve the reaction rate because the kinetics appear complex for slow reacting compounds such as 2,4-DiClDPAA. Although the products are formed by nucleophilic displacement the kinetics are not first or pseudo first order. Moreover the reaction yield does not increase as the ionic strength or as the amount of BzBr provided at least 15 uL of reagent are used. The effects of temperature are also minimal with statistically insignificant differences observed at 40°C and 50°C. This complexity of the kinetics may result from hydrolysis of BzBr to benzyl alcohol which can complicate the kinetics by two mechanisms. The first mechanism is via destruction of the reagent during by hydrolysis. This would increase with an increase in temperature thus offsetting the increase in reaction rate with temperature. A second mechanism producing reduced yield may be result from inhibition of XAD-2 supported esterification of carboxylic acids by alcohols (17). Since the reaction is slow the rate of hydrolysis of BzBr may be competitive with esterification. The resulting increase of benzyl alcohol could inhibit the reaction. This possibility is currently being investigated.

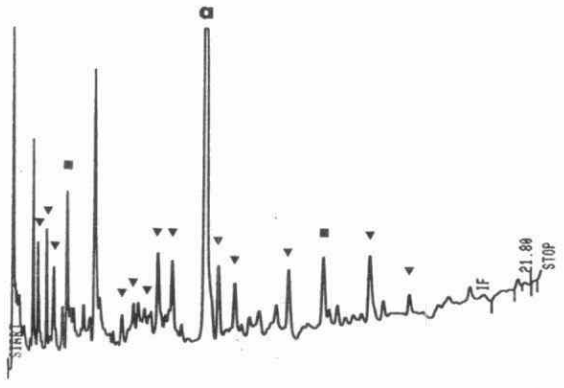


Figure 2: GC/ECD trace of an isolate from benzylation and purification of 20 mL phosphate buffer containing 3 nG/mL 2,4-DiClDPAA: (a) 2,4-DiClDPAA Bz ester; (■) solvent contaminants; (▾) cartridge contaminants.

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D16

Polyclonal and Monoclonal Immunoassays for Picloram Detection

Raymond J. A. Deschamps and J. Christopher Hall

Department of Environmental Biology, University of Guelph, Guelph, Ontario, Canada, N1G 2W1

ABSTRACT

A radioimmunoassay (RIA) and two indirect enzyme immunoassays for picloram (4-amino-3,5,6-trichloro-2-pyridinecarboxylic acid) were developed for the detection of the herbicide in river water, urine, as well as soil and plant extracts. The RIA method incorporated a novel radiolabel consisting of [^{3}H]glycine covalently linked to picloram. Using the RIA procedure, unknown picloram concentrations in the range of 50 to 5,000 ng/ml could be detected in river water and urine when a standard curve was prepared in the respective matrix. The two indirect enzyme assays were compared in terms of sensitivity, accuracy and precision for detection of unknowns in various matrices using standard curves prepared in buffer. The assay using a rabbit anti-picloram serum had a linear working range from 5 to 5000 ng/ml with I_{50} ranging from 80 to 200 ng/ml and a lower detection limit of 5 ng/ml. The assay using a monoclonal antibody obtained from a mouse hybridoma cell line yielded a linear working range from 1 to 200 ng/ml with I_{50} values ranging from 8 to 12 ng/ml and a lower detection limit of 1 ng/ml. From the analysis of fortified river water, soil extracts, plant extracts, and urine, the monoclonal antibody-based assay was shown to be more sensitive, more accurate, and more precise than the polyclonal antiserum-based assay.

INTRODUCTION

Picloram is used for the control of woody and broadleaf herbaceous plants. It is relatively resistant to breakdown in the environment and has been found to be mobile in the soil (1). Picloram residues have been found in surface and groundwater samples (2, 3). The mobility in the environment shown by picloram along with the susceptibility of certain crops to extremely small amounts of this compound (4) make monitoring water for picloram residues necessary.

In disciplines such as clinical chemistry and endrocrinology, immunochemistry is often the analytical method of choice because of its sensitivity, specificity, speed of analysis, ease of automation, cost effectiveness, and general applicability. The potential of immunochemical technology for pesticide residue analysis in various substrates such as soil, water, plants, urine, and blood has been examined by several authors (5 - 11). Many pesticides, including picloram, require an extensive sample preparation including derivatization before they can be analyzed by gas chromatography. As alternative methods, immunoassays can be sensitive, specific, and precise providing for rapid, cost effective analyses. Immunoassays may be based on polyclonal or monoclonal antibodies. The former is a heterogenous mixture of proteins isolated from serum that represents a variety of antibody molecules of differing specificities and affinities. In contrast, the latter is a homogenous reagent possessing a single antibody specificity and affinity. In a variety of assay systems, either monoclonal or polyclonal antibodies may have certain advantages over the other. For a detailed description and comparison of polyclonal and monoclonal antibodies, the reader is referred to the text by Zola (12).

The majority of published immunoassay techniques for pesticide detection employ polyclonal antibodies. In a review of immunoassays for agrochemicals, Mumma and Brady (10) cite 49 assays employing polyclonal antibodies and only 12 employing monoclonal antibodies. The reason for this discrepancy in popularity may be that polyclonal antibody-based assays, at first examination, are easier to develop. However, when used as reagents for the quantitation of pesticide

residues, monoclonal antibodies have certain advantages over polyclonal antibodies which include: i) hybrid cells can be cultured indefinitely, either in vivo or in vitro to yield a potentially unlimited supply of homogenous, standardized reagent; ii) during the hybridoma selection process, the investigator can select a hybrid cell producing the desired antibodies in terms of specificity and affinity; iii) the monoclonal antibody will be free of antibodies that are specific for irrelevant antigens which may interfere with the assay's performance; and iv) cross-reactivity with structurally similar molecules (e.g. other members of a pesticide class) can be selected for or against depending upon whether the investigator desires an assay to detect a single pesticide or a class of pesticides (13, 14). Despite these issues which favor monoclonal antibody-based assays, it is possible to develop excellent immunoassays based on polyclonal antibodies.

In this paper, we will review our previous research on a radioimmunoassay (RIA) procedure for the detection and quantitation of picloram using polyclonal antisera (15). Furthermore, we will also discuss our research on indirect EIA procedures using monoclonal and polyclonal anti-picloram antibodies which were compared in terms of the characteristics of the standard curves and performance based on the determination of picloram in fortified water, soil extracts, plant extracts, and human urine samples (16).

MATERIALS AND METHODS

Preparation of Immunogens. Picloram was conjugated to BSA as described by Hall et al. (15) and Fleeker (17). Equimolar amounts of [^{14}C]picloram (46 mg, 45.5 Bq), NHS (22 mg), and DCC (39 mg) were dissolved in the sequence given in 2.5 mL of dioxane. The solution was allowed to stand at room temperature for approximately 18 h at which time it was filtered to remove the precipitate. The filtrate was evaporated to dryness on a rotary evaporator under vacuum at 35°C. A solution of BSA (500 mg) dissolved in 3 mL of 0.10 M borate buffer (pH 9) was added to the residue and the mixture was agitated gently for 1 h at room temperature. The resulting solution was dialyzed against several changes of deionized water over 36 h at 4°C and lyophilized. The amount of herbicide bound to BSA was estimated by measuring ^{14}C present in weighed portions of product dissolved in PBS. Approximately 15 to 20 molecules of picloram were bound per BSA molecule.

Preparation of Coating Conjugates. Picloram (50 mg) was dissolved in 5 mL thionyl chloride ($SOCl_2$) in a small boiling flask. The solution was refluxed for 2.5 h at 85 °C to form the acid chloride of picloram. Excess thionyl chloride was removed under vacuum at 60 °C on a rotary evaporator. The residue was dissolved in 2 mL of tetrahydrofuran (THF). The picloram acid chloride solution was added slowly with stirring to 200 mg RSA in 10 mL of 0.02 N NaOH. Before the addition of the acid chloride solution was completed, precipitate formed which did not re-solubilize after stirring for 18 h at room temperature. Dilution of the reaction mixture to 200 mLs with 0.02 N NaOH succeeded in dissolving most of the precipitate. The resulting suspension was centrifuged to remove any precipitate. The supernatant was dialyzed against cold flowing tap water for 24 h and lyophilized.

Production of Polyclonal Anti-Picloram Antibody. Picloram antisera was obtained from New Zealand White rabbits following the protocol described by Hall et al. (15). The rabbits were injected subcutaneously with an emulsion consisting of 0.5 to 1.0 mg immunogen dissolved in 0.5 mL of PBS and an equal volume of Freund's complete adjuvant. The injections were repeated 3, 6, and 10 days after the initial injection, substituting Freund's incomplete adjuvant for complete adjuvant. A booster injection was given one month after the initial injection and was repeated at monthly intervals thereafter. The rabbits were bled for antibody titer determinations 10 days after each boost. Antisera for picloram immunoassay development were prepared from a single bleed in each case.

Production of Monoclonal Anti-Picloram Antibody. Ten 11-week-old mice were injected intraperitoneally with a total volume of 250 uL of a 1:1 (v/v) mixture of 70 ug of immunogen dissolved in phosphate buffered saline and Freund's complete adjuvant (16). Secondary inoculations were given three and eleven weeks after the initial immunization. One week following each secondary inoculation, the mice were bled from the retro-orbital plexus and the anti-picloram serum antibody titer was determined using the RIA procedure described by Hall et al. (15). A serum sample was considered positive for anti-picloram antibody activity if binding of the picloram radiolabel was more than twice the level of non-specific binding.

The spleen was removed and cut into several small pieces and was gently forced through a 400 mesh stainless steel screen into a second Petri dish which also contained RPMI medium. The cell suspension was transferred to a sterile centrifuge tube and any large tissue aggregates were removed by the sedimentation procedure described by Shortman et al. (18). The suspension was centrifuged (200 x *g*) for 10 minutes and the cell pellet was resuspended in fresh medium. Cells in trypan blue viability stain were enumerated microscopically. The spleen cells were mixed with an equal number of SP/2.0 myeloma cells in the semi-log growth phase in RPMI medium. The cell mixture was centrifuged (200 x *g*) for 10 minutes and the cell pellet was suspended in 1 mL of polyethylene glycol (3 000 - 4 000 mol. wt. range) at 37 °C. The suspension was mixed continuously for one minute, followed by the addition of 1 mL of RPMI medium and another one minute of continuous mixing. An additional 9 mL of RPMI medium was added slowly with mixing. The fusion products were centrifuged at 200 x *g* for 10 min, the supernatant discarded, and the cell pellet resuspended in RPMI medium supplemented with 10% fetal bovine serum, 10% NCTC-109 medium and 1% HAT. The cell suspension was dispensed (100 uL/well) into six sterile 96-well microtitration plates. The plates were incubated at 37 °C in an atmosphere of 5% CO_2 in air.

The culture showing the best results from an EIA assessment designed to detect the presence of picloram specific antibodies was selected for the limiting dilution procedure to acheive the clonality of the hybridoma cells. A dilution was calculated to yield one cell per well of a 96 well microtitration plate. The wells of the plate were checked daily for the presence of a single colony. Once a colony was visible, it was fed with 125 uL of RPMI medium. Supernatant (125 uL) was removed from the well for screening by EIA when the cells of the colony were one-quarter to one-half confluent. Cells from colonies testing positive for anti-picloram antibody activity were transfered to 24 well plates, rescreened by EIA and transfered again into 25 cm^2 flasks if they remained positive for picloram antibodies. The limiting dilution procedure was repeated to ensure monoclonality. After a final assessment by EIA, the cells producing the monoclonal antibodies specific for picloram were collected for the production of ascitic fluid in mice.

Mice were given an injection of 0.5 mL pristane (2,6,10,14-tetramethylpentadecane), a hybridoma growth promoting compound. Seven days later, the mice were injected with 3 x 10^6 hybridoma cells in 200 uL of PBS supplemented with 5% fetal bovine serum. Approximately two weeks following the injection of cells, ascites fluid was withdrawn, centrifuged to remove red blood cells, and frozen at -20 °C until used.

Preparation of Radiolabel. The mixed anhydride of picloram was prepared by adding picloram (6 mg), triethylamine (5 uL), and isobutyl chloroformate (5 uL) in the sequence given to 500 uL of dioxane. A portion of the mixed anhydride solution (100 uL) was added to a solution of 100 uL of [^{3}H]glycine (0.1 mCi), 100 uL of dioxane, 100 uL of distilled water, and 2 uL of 2 M NaOH. After 1 h, an additional 2 uL of NaOH was added. The reaction was allowed to proceed for a total of 4 h at room temperature.

The picloram-[^{3}H]glycine conjugate was isolated and purified by

chromatography on silica gel TLC as described by Hall et al. (15) using the solvent system 60:40:2 diethyl ether: petroleum ether: formic acid (v/v/v).

Sample Preparation. Water was collected from the Speed River, Guelph, Ontario and stored at 4 °C. The water was fortified with an acetone solution of picloram. Soil (40 g) was shaken 15 min with 200 mL of a 1:1 methanol/water solution. The mixture was filtered through a glass fibre filter and the methanol was removed under vacuum at 50 °C. The volume of the resulting aqueous solution was returned to 100 mL with Pi buffer (0.1 M phosphate, 1 mM $MgCl_2$, pH 7.5) and filtered through a 0.45 um nylon filter. The filtered extract solution was fortified with an acetone solution of picloram. Grass clippings (20 g) were homogenized in 100 mL of 0.1 N KOH with 10% KCl. The homogenate was shaken for 30 min and filtered through a glass fibre filter. The filtrate was acidified to pH 2 with 3 N H_2SO_4, refrigerated at 4 °C for 30 min and centrifuged at 3000 x *g* for 10 min. The volume of the supernatant was made up to 100 mL with Pi buffer and aliquots were fortified with an acetone solution of picloram. Prior to analysis, 10.00 mL of the fortified solution was forced through a C_{18} reversed phase liquid chromatography column. The column was washed with 5 mL of water and dried with a gentle stream of forced air for 1 min. The column was eluted with 9 mL of methanol. The eluate was evaporated to dryness and the residue was redissolved in 10.00 mL of Pi buffer. Human urine was fortified with picloram and 10 mL aliquots were acidified to pH 2 with 3 N H_2SO_4. The picloram was extracted three times with 3 mL portions of diethyl ether. The ether fractions were pooled and evaporated to dryness. The residue was redissolved in 10 mL Pi buffer, and cetrifuged at 12 000 x *g* for 10 min.

Recoveries for the extractions described above were determined using [^{14}C]picloram added to soil, grass clippings, and urine, respectively. Recoveries were 95% for the soil extraction, 90% for the plant extraction and 90% for the urine extraction.

Indirect Enzyme Immunoassay. The following procedure is a modified version of that described by Deschamps et al. (16).

Microtitration plates were coated by adding to each well 100 uL of coating conjugate dissolved in Pi buffer (0.1 ug coating antigen per mL). The plates were incubated overnight at 4 °C. The plates were emptied and washed three times with washing solution (Pi buffer supplemented with 0.1% Tween 20). If the plates were not to be used immediately, they were wrapped with plastic and and stored at 4 °C for up to 24 h.

Sites on the polystyrene well surface unoccupied by coating conjugate were blocked by adding 200 uL of 0.1% (w/v) gelatin solution in Pi buffer and incubated for 20 min at 4 °C. The plates were emptied and washed as described above.

Antiserum diluted 1 to 20 000 or ascites fluid diluted 1 to 10 000 in Pi buffer supplemented with 0.05% Tween 20 surfactant (5) were preincubated 1:1 (v/v) with picloram standard or sample solutions. Aliquots of the preincubated mixture were transfered to the wells of the microtitration plate (200 uL per well). The plates were incubated for 1 h at 4 °C.

After washing the plates as before, 200 uL of goat anti-rabbit or goat anti-mouse IgG-horseradish peroxidase conjugate diluted 1 to 5000 in Pi buffer was added to each well and the plates were incubated for 1 h at 4 °C, emptied and washed.

Substrate (1 mg/mL ABTS, 1 mg/mL urea hydrogen peroxide in citrate buffer: 0.024 M citrate, 0.047 M phosphate, pH 5.0) was added and color was allowed to develop for 30 min. The color reaction was stopped by the addition of 100 uL 0.5 M citric acid. Absorbance of each well was measured at 405 nm with a microtitre plate reader. Absorbance values of the standards and the

samples (A) were divided by the maximum absorbance value (A_o) representing those wells in which binding of antibody to the coating conjugate was not challenged with free picloram in solution. The A/A_o values for standards were plotted against the log of picloram concentration to construct a standard curve. Concentrations of samples were calculated on the basis of the standard curve.

RIA Procedure. The RIA procedure described by Hall et al. (15) was used. Into 1.5 mL microcentrifuge tubes was transfered 100 uL of standard or sample. Incubation mix (300 uL per tube) consisting of one part deionized water, one part inert serum, 12 parts PBS, and sufficient radiolabel to yield 10,000 cpm per assay was added to each tube. Antisera diluted in PBS was added to the tubes (100 uL per tube). One set of control tubes did not receive antisera for determination of non-specific binding and a second set of control tubes received antisera only for maximun binding of radiolabel (B_o). The contents of the tubes were mixed thoroughly, incubated at 4°C, the antibody-bound radiolabel fraction precipitated with $(NH_4)_2SO_4$, centrifuged, and the pellet dissolved in water prior to assaying for radioactivity.

All results were corrected for non-specific binding. Values for standards were divided by B_o and were plotted against the log of the herbicide concentration (ng/mL). The quantity of the herbicide in the unknown sample was calculated based on the standard curve.

RESULTS AND DISCUSSION

A linear relation between the log of picloram concentration and relative binding (B/B_o) was found in the range of 50 to 5,000 ng/mL of picloram for the RIA procedure (Figure 1). The coefficient of variation within a run was 3% or less for picloram determined by the RIA method.

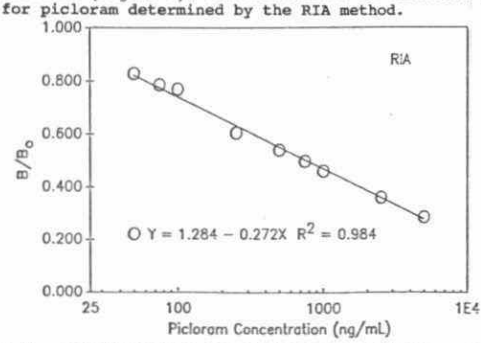

Figure 1. Standard curve for picloram quantitation using radioimmunoassay.

Recoveries from fortified river water and human urine samples determined by the RIA were good with mean overall recoveries varying from 82% to 110% (Table I). The range of concentrations over which picloram was accurately quantitated with no sample clean-up correspond with levels found in urine in applicator exposure studies conducted by Libich et al. (19). It must be emphasized that determination of unknown concentrations of picloram in river water and urine was performed by using standard curves prepared in the respective matrix.

Table I. Recovery of Analyte from River Water and Human Urine Samples as determined by RIA.

Method	Analyte	Amount of analyte added, ug/mL	Recovery[a] River water	Human urine
RIA	picloram	0.25	0.25 ± 0.03 (6)	0.19 ± 0.04 (6)
		2.50	2.60 ± 0.19 (6)	2.22 ± 0.35 (6)

[a]Mean recovery: ug/mL ± SE (number of determinations).
[b]ND = not determined.

The RIA methods reported here incorporate a novel radiolabel. Herbicides labelled with ^{14}C are easily obtained but do not lend themselves to sensitive and accurate immunoassay work because of low specific activities (8). Radioimmunoassays utilizing high specific activity radiolabels such as [^{3}H]2,4-D (20) or an [^{125}I]2,4-D derivative (21) have given good results. Covalently linking picloram with [^{3}H]glycine yields a radiolabel with high specific activity without the expense of purchasing a custom synthesized tritiated herbicide or the health hazards connected with iodated radiolabels.

In another set of experiments, picloram standards in Pi buffer were used to generate standard curves for comparison of two indirect EIA procedures in which polyconal and monoclonal antibodies were used, respectively. A linear relation between the log of picloram concentration and relative absorbance (A/A_o) was found in the range 5 to 5000 ng/mL for the polyclonal assay and 1 to 200 ng/mL for the monoclonal assay. The monoclonal assay, therefore, had a standard curve with a much steeper slope compared to the polyclonal assay. Typical coefficient of determination values (r^2) were 0.97 for the monoclonal assay and 0.95 for the polyclonal assay.

The polyclonal assay had an I_{50} value in the range 80 to 200 ng/mL with a lower detection limit of 5 ng/mL. The monoclonal assay was more sensitive with an I_{50} value ranging between 8 and 12 ng/mL and a lower detection limit of 1 ng/mL. Both assays were more sensitive than the RIA for picloram which had an I_{50} value of 760 ng/mL and a lower detection limit of 50 ng/mL (15).

Using the absorbance values of the picloram standards, the interwell variability was determined for the two EIA procedures. The polyclonal assay showed a mean interwell coefficient of variation (CV) of 6.4% over the standard curve. The mean interwell CV over the standard curve for the monoclonal assay was slightly lower at 5.3%. Interassay CV of the picloram standard A/A_o values determined on four separate runs for the polyclonal assay ranged from 2.1 to 23% with a mean of 12.8%. For the monoclonal assay, the interassay CV of A/A_o values determined on seven separate occasions ranged from 5.1 to 26% with a mean of 16%. In both cases, CV values increased with an increase in picloram standard concentration due to decreasing A/A_o values. Singh et al. (22) showed similar results for their enzyme immunoassay for the antibiotic sulfamethazine. Intrassay CV values were obtained on picloram determinations in four fortified plant extract samples. The polyclonal assay showed a much higher variability with a mean CV value of 80% over the four plant extract samples compared to only 19% for the monoclonal assay over the same samples (Table II).

Three structurally related pyridine herbicides, clopyralid, fluroxypyr, and triclopyr were tested for cross-reactivity with the polyclonal and monoclonal anti-picloram antibodies. Neither antibody cross-reacted appreciably with the other pyridine herbicides as the I_{50} values in all cases were greater than the highest concentration of herbicide tested (50 000 ng/mL

for the polyclonal antibody, 10 000 ng/mL for the monoclonal antibody).

Table II. Intraassay Variability of Picloram in Four Fortified Plant Extract Samples from Enzyme Immunoassay Standard Curve using Polyclonal or Monoclonal Antibodies.

Picloram added, ng/mL	Picloram recovered			
	PcAb EIA[a] mean, ng/mL	CV, %	McAb EIA[b] mean, ng/mL	CV, %
4	9.9	87	3.9	29
20	39	89	24	15
40	99	84	52	21
400	780	59	90[c]	10

[a]Polyclonal antibody enzyme immunoassay.
[b]Monoclonal antibody enzyme immunoassay.
[c]1/5 dilution.

Recovery of picloram from water, soil extracts, plant extracts, and urine indicated that the monoclonal assay was far superior for quantitative determinations (Tables III, IV). Overall recoveries for the monoclonal assay were 78, 73, 112, and 167% for water, soil extract, plant extract, and urine, respectively. For the polyclonal assay, overall recoveries were 200, 388, and 221% for water, soil extract, and plant extract. The polyclonal assay for determination of picloram in urine was not successful because of unacceptable interference from an unknown contaminant. Picloram concentration estimates were taken from a standard curve made in Pi buffer. Interference from components of the sample matrix likely accounts for much of the error in the concentration estimates. Such interferences from sample components have been reported by Wie and Hammock (23). In preliminary studies, we have found that if a sample has a higher ionic strength than the solution used for the standards, the picloram concentration of the sample will be consistently overestimated. In the reverse situation, concentrations of the sample will be underestimated. We also found that these effects could be minimized if the antibodies were diluted in Pi buffer supplemented with 0.05% (v/v) Tween 20 as described by Hunter and Lenz (9). Singh et al. (22) determined sulfamethazine in swine plasma using a standard curve also based on plasma with excellent accuracy. The RIA procedure for picloram in water and urine using the same polyclonal antisera as in the EIA described here showed a high degree of accuracy (82 to 110% recovery) when the standard curves were constructed using blank water or urine. We chose not to do this for the indirect monoclonal and polyclonal procedures for the following reason. Soil or water samples from different geographical regions or urine samples from different subjects will vary widely in composition. Selecting one blank water or soil sample to use for the standard curve would not be appropriate and attempts to obtain an "average" water or soil sample would be difficult. It is evident that this choice had more severe consequences with respect to the polyclonal antibody-based assay than with the monoclonal antibody-based assay. The advantage of a standard curve with a steep slope is that small errors in absorbance values will not translate to large errors in concentration estimates.

One disadvantage of a standard curve with a steep slope is the narrow linear working range. Rather than making several dilutions of a sample in the hope of obtaining one dilution in the proper range, it may be more efficient to conduct a separate assay with a wide working range to rank samples so that appropriate dilutions can be made with certainty for accurate quantitation by a second assay. The polyclonal system described here would be adequete for the

role of ranking samples. Alternatively, one could modify the parameters of the monoclonal assay (e.g., increase the antibody concentration) to achieve a standard curve with a flatter slope and a wider working range.

Table III. Recovery of Picloram from Fortified Water, Soil and Plant Samples Determined by Enzyme Immunoassay using Polyclonal or Monoclonal Antibodies.

Picloram added, ng/mL	Picloram recovered, ng/mL[a]	
	PcAb EIA[b]	McAb EIA[c]
Fortified water		
20	27 ± 5.1 (18)	11 ± 0.98 (12)
200	569 ± 79 (18)	165 ± 7.4 (12)
2000	3590 ± 550 (18)	96 ± 4.0 (12)[d]
Fortified soil		
4	23 ± 4.4 (24)	2.1 ± 0.15 (36)
20	90 ± 23 (24)	13 ± 0.53 (36)
40	110 ± 23 (24)	33 ± 1.1 (36)
400	1010 ± 280 (24)	97 ± 2.5 (12)[d]
Fortified plant extract		
4	9.9 ± 2.5 (12)	3.5 ± 0.23 (24)
20	39 ± 10 (12)	24 ± 1.0 (24)
40	99 ± 24 (12)	51 ± 2.4 (24)
400	780 ± 130 (12)	90 ± 2.6 (24)[d]

[a]Mean ± SE (number of determinations).
[b]Polyclonal antibody enzyme immunoassay.
[c]Monoclonal antibody enzyme immunoassay.
[d]1/5 dilution.

Table IV. Recovery of Picloram from Fortified Human Urine Samples Determined by Enzyme Immunoassay using a Monoclonal Antibody[a].

Picloram added, ng/mL	Picloram recovered, ng/mL[b]
	McAb EIA[c]
4	11 ± 0.58 (12)
20	30 ± 2.2 (12)
40	50 ± 2.1 (12)
400	90 ± 2.5 (12)[d]

[a]Polyclonal assay was not successful due to unknown contaminant.
[b]Mean ± SE (number of determinations).
[c]Monoclonal antibody enzyme immunoassay.
[d]1/5 dilution.

It is commonly stated that for polyclonal antibody production, the design and the preparation of the immunogen are most critical (7, 8, 24). Several studies have illustrated the influence of hapten structure, bridging groups, immunogen structure, and coating conjugate structure on immunoassay performance (25 - 27). The goal of immunogen design and preparation is to maximize the quantity of specific antibodies in the antisera having high affinity for the antigen (analyte). In general, one advantage of the monoclonal technique over polyclonal antibody production is that the antigen does not have to be pure for the purposes of immunization as long as during the screening process, high

affinity antibodies specific for the antigen of interest can be distinguished from low affinity antibodies and those that are specific for irrelevant antigens. Likewise, the design of the immunogen used to produce monoclonal antibodies may not be as critical as that required for polyclonal antibody production. An effective screening program will enable the investigator to select and expand the hybridoma cell clone(s) producing the desired antibody even if such clones are rare. In the present study, the same immunogen that yielded a polyclonal antisera with a low average affinity also yielded a monoclonal antibody of high affinity.

The immunoassays reported here could be incorporated on a routine basis in most laboratories to serve one of two functions. The assays could be used as a rapid, inexpensive method for herbicide quantitation with little or no sample clean-up. Alternatively, they may be implemented as a preliminary screen to rank samples for follow-up determination by gas chromatography. In either function, the immunoassays represent savings in time, labor, and materials.

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DETERMINATION OF THE TRULY DISSOLVED CONCENTRATION OF ORGANIC CONTAMINANTS BY HEADSPACE ANALYSIS

by

J. Resendes*, W. Y. Shiu and D. Mackay

Department of Chemical Engineering

University of Toronto

Introduction

Headspace analysis of the air phase in equilibrium with aqueous solutions of hydrophobic organic chemicals is being used to determine the truly dissolved concentration of organic contaminants in the aqueous phase. This permits evaluation of the extent to which hydrophobic organic chemicals interact with dissolved and particulate organic matter in water. The technique is also being used to elucidate the "solids concentration effect" which was first demonstrated by O'Connor and Connolly (1) who observed that the sorbed phase - water partition coefficient Kp appears to vary with the particulate organic matter (solids) concentration i.e. as the solids concentration increases, Kp tends to fall. It has been proposed that this phenomenon arises from the presence of a third colloidal phase, which is "wrongly" analyzed as being in solution. Others believe that the cause is enhanced desorption due to the increase in the solids concentration.

The attractive feature of this analytical technique is that by analyzing the air phase the fugacity of the chemicals in the water phase are determined indirectly and without disturbing

the system. It is believed to be superior to techniques involving filtration or centrifuging. Investigation into this area is needed to obtain an improved understanding of the extent to which organic chemicals are sorbed in water so that more reliable assessments of water column processes such as volatilisation, bioaccumulation and sedimentation can be made. A knowledge of these processes is, in turn, important for water quality assessments.

Data are being obtained on the sorption partition coefficients of various hydrophobic organic chemicals to different organic matrices, including alcohols, humic and fulvic acids and naturally occurring dissolved organic carbon (DOC). The ultimate goal is to develop procedures whereby the extent of binding, sorption or interaction of these chemicals to these phases may be ascertained.

The system which has been designed to accomplish this is described here and selected results are presented for chlorobenzenes interacting with a variety of organic material.

Theoretical Principles

The system described below enables a mixture of known composition of water, volatile solute and sorbent or cosolvent to be prepared, then the equilibrium air phase concentration can be measured by a GC. In principle, the concentration can be converted into a partial pressure or fugacity f_{ai} in the air phase which can be equated to the fugacity of the chemical in the aqueous phase f_{wi}. Now

$$f_{ai} = f_{wi} = x_i * g_i * f_{ri}$$

where x_i is the mole fraction of the chemical in the water, g_i is its activity coefficient on a Raoult's Law basis and f_r is the reference fugacity or the fugacity of the pure liquid chemical at the system temperature and is equal to the liquid vapour pressure.

Measurements of air water partition coefficients or Henry's Law constants (HLC) enable g_i and f_{ri} to be deduced from

$$P_{ai} = H_i * C_{wi}$$

where P_{ai} is partial pressure (Pa) and can be equated to fugacity, C_{wi} is concentration in water (mol/m^3) and H_i is the HLC (Pam^3/mol). Now P_i is equal to f_{ai} and C_{wi} is x_i/v_w where v_w is the molar volume of the solution (generally 18E-6 m^3/mol), thus

$$H_i = g_i * f_{ri} * v_w$$

The dimensionless air-water partition coefficient K_{aw} is given by

$$K_{aw} = C_a/C_{wi} = (P_a/RT)/C_{wi} = H_i/RT$$

where R is the gas constant (8.314 $Pam^3/molK$) and T is the absolute temperature. It follows that if H or K_{aw} is known then if P_{ai} is measured C_{wi} or x_i can be deduced. There are believed to be two types of association of chemical with other material in the water column.

Second Phase Association

In this case a second solid or liquid phase is present in which the chemical sorbs or dissolves. If the volume fraction of this phase is F and the total chemical concentration is C_t,

then it can be shown that in the experimental system described below a plot of the ratio of initial partial pressure to partial pressure or initial area counts to area counts will have a slope of approximately (K_{pw} - 1) where K_{pw} is the partition coefficient between the second phase and water. This is illustrated in figure 2 for 1,2-diCB and octanol as cosolvent.

Dissolved Phase Association

In this case a "cosolvent" such as an alcohol is added which is truly dissolved. It can be shown that the corresponding plot of partial pressure or fugacity or area counts ratio will have an initial slope of approximately $-\ln K_{pw}$ where K_{pw} is here the ratio of solubility in cosolvent to that in water.

Addition of a partially miscible cosolvent eg. octanol or benzene is thus expected to have a low initial slope of $-\ln K_{pw}$ then at the onset of phase separation the negative slope will increase markedly to $-(K_{pw}-1)$.

We can thus test natural organic matter eg. DOC, fulvic, humic acids to determine the contribution of truly dissolved and second phase material by observing the slope of the area counts vs F plot.

Examination of data from Kile and Chiou (2) suggests that fulvic acids are behaving like a second phase because the slope is large ie. K_{pw} is similar in magnitude to K_{ow} and much greater than $_{i}nKp_{w}$ but the organic matter is undoubtably dissolved and not filterable. We thus have dissolved second phase material. Experimentally the only way to probe or sense this behaviour is by making measurements of the solubility or fugacity. Filtering and centrifuging are totally ineffective. We thus believe that the system being devised has potential to identify the true condition of hydrophobic organic chemicals in a water column, thus adding a new investigative tool for water quality analysis. It has potential to provide more valuable and

reliable information on the condition of hydrophobic organic chemicals.

Experimental

Equipment

The apparatus for the headspace analysis in this study consists of a closed system made up of a 2.8 L water jacketed glass vessel, a metal bellows pump (Metal Bellows Corp., model MB-21) and an 8 port 1/8" UWP series Valco gas sampling valve with 1 cc loops. The units are joined by 3.2 mm OD (1/8") stainless steel (SS) tubing. An HP5890 gas chromatograph with a J&W Scientific fused silica DB-17 capillary column and electron capture detection is used for analysis. A SGE OC1-3 on-column injector is used. Helium is used as a carrier gas and argon/methane as the make up gas. A Neslab RTE-110 water bath with proportional temperature control is also used.

Figure 1 is a drawing of the system. The 3.2 mm OD (1/8") SS tubing is wrapped with heating tape to reduce adsorption of chemicals to the lines. The valve is heated by a cartridge heater connected to the valve body inside an insulated box. The valve was originally connected to the on-column injector of the GC by 1.6 mm OD (1/16") SS tubing. The on-column injector was removed in latter experiments and the valve directly connected to the column with a piece of 0.53 mm ID deactivated fused silica tubing.

Materials

The chlorobenzenes used are 1,2-diCB, 1,2,4-triCB, 1,2,3,5-tetraCB and pentaCB. Hexanol, octanol and benzene were used as co-solvents. Humic acid is also used. The water used in the experiments consisted of tap water purified by reverse osmosis and further treated by a Millipore Milli-Q Water Purification System.

Method

The chlorobenzenes were chosen on the basis of their sensitivity to ECD and their low solubilities. A series of standard solutions were prepared and samples injected into the on-column injector with a Hamilton syringe with fused silica needle. The results showed linear detector response. The vessel system was also calibrated after the on-column injector was removed. Linear detector response was also observed. Analysis of the headspace is accomplished by switching the valve from one position to the other. The valve schematic is shown in figure one. In either of the two positions there is air from the vessel going through one loop and carrier through the other. By turning the valve to the other position the order is reversed and a 1 cc sample is sent to the GC.

For the co-solvent experiments, two liters of purified water were put in the vessel and the system connected and sealed. The chlorobenzenes were added in "saturated" solution form to the vessel with a gas tight syringe. The "saturated" solutions were actually below saturation and were prepared in separate batchs.

After adding the saturated solutions to the vessel the system was allowed to equilibrate (4-5 hours or overnight). The headspace was then analyzed. Seven or more samples were chromatographed over periods of three hours or more to ensure equilibrium had been reached. Hexanol, octanol and benzene were used separately in the co-solvent experiments. A small amount of co-solvent was added to the vessel by gas tight syringe. The system was allowed to equilibrate and the headspace analyzed. Addition of co-solvent and equilibration was repeated until approximately twice the amount needed for saturation was added.

Results and Discussion

Figure 2 contains the results of the 1,2-diCB - octanol experiment (second phase region). The slope is predicted to be K_{pw} - 1. Since the cosolvent used was octanol, K_{pw} should also be K_{ow}. By linear regression of the graphical data the slope is 2670. K_{ow} is 2500 for 1,2-diCB. The model therefore correctly predicts the experimental behaviour. The results of the dissolved phase region of the same experiment are shown in figure 3. The slope is predicted to be $-\ln K_{pw}$ which for 1,2-diCB is -7.83. The slope from the graph is -212. There is greater enhancement occurring than is predicted by the model equation.

Figure 4 shows the results of the 1,2-diCB - benzene experiment (miscible region). A straight line with correlation coefficient (r) of 0.98 was found for the data. The slope was found to be -99 which again shows the limitations of the model in the dissolved phase region..

Figure 5 contains the results of the 1,2,3,5-tetraCB - humic acid experiment. The results point out that humic acid acts as a second phase and the partition coefficient K_{pw} can be obtained from the slope (1.63e4).

Conclusions

1 The experimental technique that has been devised has permitted a precise way of investigating solubility enhancement especially by humic substances.

2 More studies are needed of the dissolved phase region of the cosolvents.

3 The system is limited to more volatile chemicals. It is desirable to work with PCB's. System modifications such as using glass lined tubing are desirable.

Acknowledgements

We would like to acknowledge the Ontario Ministry of the Environment for the financial support of this project and especially Bill Berg and Youseri Hamdy.

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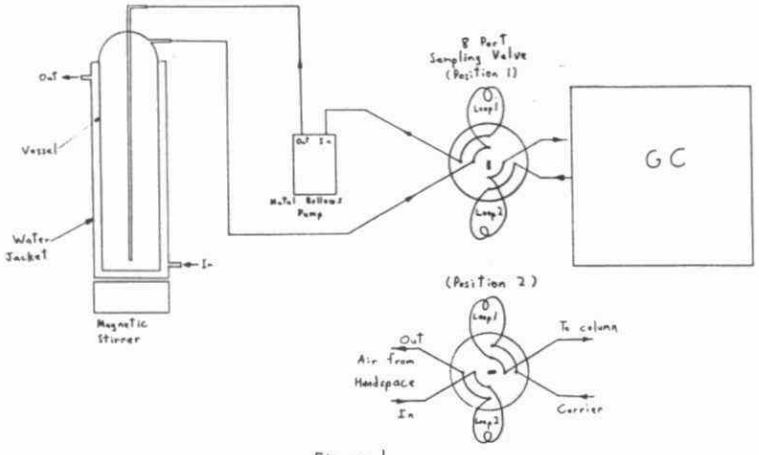


Figure 1

Figure 2 Octanol Cosolvent Experiment

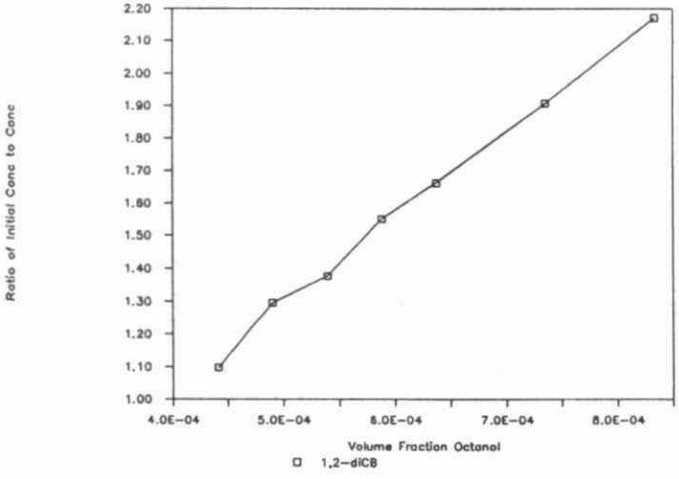


Figure 3 Octanol Cosolvent Experiment

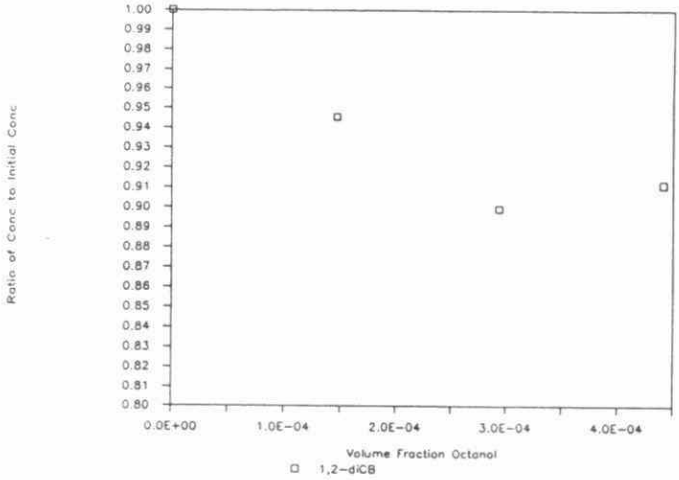


Figure 4 Benzene Cosolvent Experiment

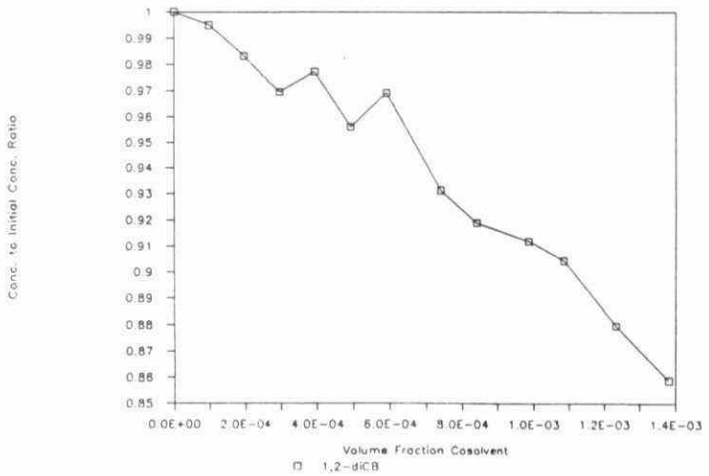
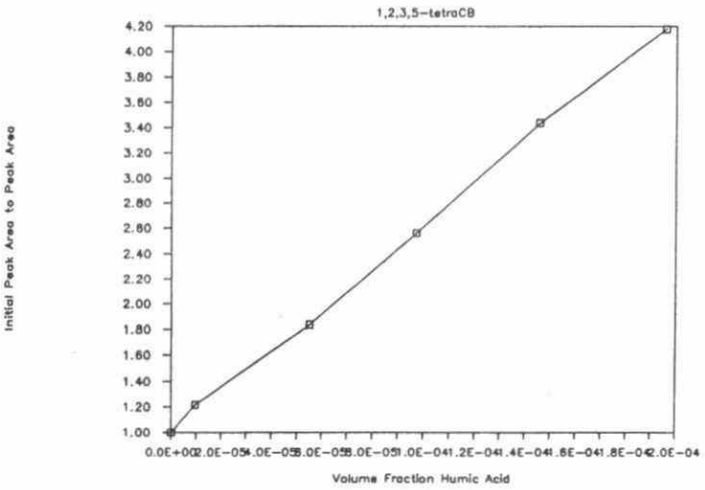


Figure 5 Humic Acid Experiment



D18

SOLID PHASE EXTRACTION OF TRIAZINES AND ORGANOPHOSPHOROUS COMPOUNDS FROM DRINKING WATER.

W.G. Craig, J.M. Craig, and A.L. Masse, Paracel Laboratories Ltd., Nepean, Ontario, K2G OG3 and C.D. Hall, Laboratory Services Branch, Environment Ontario, Rexdale, ON, M9W 5L1.

The objective of this work was to determine the feasibility of using solid phase extraction (SPE) for the analysis of organophosphorus compounds and triazines present in water. Current methodology involves the liquid liquid extraction (LLE) of the organophosphorous compounds at neutral pH using dichloromethane. A separate LLE using dichloromethane at pH 12 is necessary for the triazines.

The LLE methodology is well established but suffers from the fact that the "wet chemistry" can not easily be automated. It is time consuming, requires extensive labour, and large amounts of expensive and toxic solvents. Our earlier work with the application of SPE to chlorophenols and phenoxyacid herbicides, and, also, to polyaromatic hydrocarbons showed that for these compounds SPE tended to have higher recoveries and lower standard deviations than LLE and led us to believe that SPE might also be applicable to triazines and organophosphorous compounds.

The objective of this research was the development of a simple, rugged method that would be amenable to the eventual introduction of robotics and that would allow the simultaneous analysis of both triazines and organophosphorous compounds in drinking water. In the course of the project, parameters investigated included:

1) **The solid phase and eluting solvent.** Phenyl, cyclohexyl, octadecyl and cyanopropyl phases and the three eluting solvents, methanol, hexane and ethyl acetate were evaluated. The best combination was the octadecyl phase using ethyl acetate as the eluting solvent. Elution with hexane gave low recoveries with all phases. Elution with either methanol or ethyl acetate gave poor recoveries with both the cyanopropyl and cyclohexyl phases, moderate recoveries with the phenyl phase, and highest recoveries with octadecyl packings.

2) **Columns from different manufacturers.** Octadecyl columns manufactured by Baker, Supelco, Waters, Analytichem and Alltech were tested using ethyl acetate as the eluting solvent. Under these particular conditions, the columns manufactured by Alltech exhibited lower recoveries than the others but the remaining four were comparable to each other.

3) **Consistency of recoveries.** The recoveries over a one hundred fold range of analyte concentrations (e.g., from 50 to 5000 ng/L for atrazine and 20 to 2000 ng/L for parathion) were found to be consistent.

4) **Different matrices.** The recoveries from each of the natural waters; Verner raw water, Lakeview raw water, Ottawa city tap water, and a drilled rural well, and from one reference water (supplied by Dr. Brian Hollebone of Carleton University) were determined at pH 12. The recoveries were high for the triazines but much more variable for the organophosphorous compounds. Later work indicates that much of the variability for the organophosphorous compounds was due to the high pH.

5) **Effect of pH.** Recoveries were determined at both pH 7 and pH 12. The triazines had high recoveries at both pHs whereas those of the organophosphorous compounds were much greater at pH 7.

6) **Effect of Storage.** The stability of analytes at two different concentrations adsorbed onto an octadecyl solid phase and stored for times of one day, one week, one, two and three months at room temperature prior to elution were investigated. The adsorbed triazines were stable over this time period whereas the recoveries of the organophosphorous compounds steadily decreased with time. For example, the percentage recoveries of atrazine, alachlor, diazinon and parathion decreased from 105, 112, 101 and 103 following one day of storage to 86, 96, 45 and 36 after three months of storage, respectively.

7) **Addition of methanol to the aqueous phase.** It has been reported in the literature that the addition of ten percent methanol to the aqueous phase prior to extraction improves the recoveries of the triazines. Under our conditions, recoveries decreased slightly on the addition of methanol.

8) **Levels of interferences.** When SPE is applied to the analysis of chlorophenols and phenoxyacid herbicides in water using an electron capture detector for quantitation, interferences are significant. Throughout the course of this work (which used a thermionic specific detector) interferences were not a significant problem, although an occasional low level interference with bladex was noted.

9) **Real samples.** Fortified samples of Ottawa City Tap Water and Rideau River Raw Water at pH 7 were extracted and analyzed the same day. The results appear in Tables 1 and 2.

Table 1: Recoveries (%) of Triazine Herbicides and Organophosphorous Compounds from Ottawa City Tap Water at pH 7 using SPE with an Octadecyl 500 mg Column

Compound	Concentration (ug/L)	Replicate 1	Replicate 2	Replicate 3	Replicate 4	Replicate 5	Mean	Standard Deviation
Dichlorvos	1.00	103.5	106.3	112.2	126.0	100.0	109.6	9.1
Mevinphos	1.88	116.2	116.0	125.6	143.3	111.0	122.4	11.5
Phorate	0.38	99.2	96.1	108.3	116.4	94.8	103.0	8.2
Atraton	6.25	109.9	98.2	116.5	124.2	91.8	108.1	11.8
Diazinon	1.00	110.4	105.3	117.7	128.8	101.7	112.8	9.7
Propazine	7.50	110.5	100.1	115.3	119.4	93.5	107.8	9.6
Atrazine	6.25	110.9	101.8	114.0	121.4	94.9	108.6	9.3
Simazine	2.50	111.2	102.6	116.3	125.0	94.2	109.8	10.7
Reldan	1.88	94.8	85.6	98.7	106.2	83.4	93.7	8.4
Ronnel	1.88	79.3	73.8	81.6	91.8	67.8	78.9	8.0
Alachlor	5.00	111.2	100.6	113.8	119.7	93.5	107.8	9.4
Ametryne	4.38	109.3	96.4	111.3	120.2	89.7	105.4	10.9
Sencor	5.00	110.0	98.8	114.7	120.2	92.1	107.2	10.3
Dursban	3.13	70.0	63.1	71.5	82.0	59.4	69.2	7.8
Malathion	1.88	105.8	98.6	118.7	124.6	94.1	108.4	11.6
Parathion	0.38	107.7	99.3	113.1	119.6	91.3	106.2	10.0
Bladex	3.75	108.8	93.1	114.6	118.7	85.9	104.2	12.6
Methyl Trithion	11.25	78.9	68.3	83.4	92.3	63.9	77.3	10.2
Ethion	3.75	60.5	53.3	62.6	75.2	49.4	60.2	8.9

Table 2: Recoveries (%) of Triazine Herbicides and Organophosphorous Compounds from Rideau River Raw Water at pH 7 using SPE with an Octadecyl 500 mg Column

Compound	Concentration (ug/L)	Replicate 1	Replicate 2	Replicate 3	Replicate 4	Replicate 5	Mean	Standard Deviation
Dichlorvos	1.00	82.4	89.1	87.7	96.7	109.2	93.0	9.3
Mevinphos	1.88	97.3	114.2	103.9	121.2	134.1	114.1	12.9
Phorate	0.38	90.4	101.3	89.0	107.7	112.6	100.2	9.3
Atraton	6.25	112.4	104.4	101.3	107.8	126.2	110.4	8.7
Diazinon	1.00	105.6	115.5	103.0	122.9	127.4	114.9	9.5
Propazine	7.50	108.5	109.1	100.1	113.9	121.2	110.5	6.9
Atrazine	6.25	111.6	110.9	103.3	116.1	127.6	113.9	8.0
Simazine	2.50	110.6	107.2	101.3	113.2	126.5	111.7	8.4
Reldan	1.88	107.6	105.2	98.9	113.7	124.7	110.0	8.7
Ronnel	1.88	95.4	96.0	89.7	100.2	113.6	99.0	8.0
Alachlor	5.00	110.8	107.9	100.2	109.9	124.2	110.6	7.7
Ametryne	4.38	110.5	102.0	97.4	106.1	120.6	107.3	7.9
Sencor	5.00	112.2	107.5	100.1	111.3	119.9	110.2	6.4
Dursban	3.13	90.8	90.4	82.0	91.6	103.1	91.6	6.7
Malathion	1.88	110.3	105.9	103.0	109.8	129.3	111.7	9.2
Parathion	0.38	109.0	103.6	98.3	106.8	127.0	108.9	9.7
Bladex	3.75	110.6	92.5	87.9	94.6	118.7	100.9	11.7
Methyl Trithion	11.25	87.4	73.4	75.3	75.7	96.9	81.7	9.0
Ethion	3.75	71.3	67.5	68.9	69.4	88.5	73.1	7.8

The parameters investigated during the course of this work led to the development of the following method for the SPE of triazines and organophosphorous compounds.

Recommended Method for the SPE of Triazines and Organophosphorous Compounds

1. Determine the pH of the sample. If less than 7, increase the pH to 7 using 1 N potassium hydroxide solution.
2. Condition 500 mg C-18 columns by passing an aliquot of methanol (5 mL), followed by distilled water (5 mL) at a moderate flow rate. Do not allowed the columns to dry out.
3. Pass the sample (800 ml) through the column with vacuum assistance. Remove the vacuum from the apparatus following passage of the sample to prevent evaporative losses due to excessive air passage.
4. Centrifuge the columns briefly to remove excess water.
5. Slowly elute the analytes with 3 mL of ethyl acetate.
6. Quantitate using a gas chromatograph equipped with dual capillaries and thermionic specific detectors.

Conclusions:

Solid phase extraction allows the simultaneous determination of organophosphorous compounds and triazines in drinking waters. The method has consistent and high recoveries and low standard deviations, is rapid and easy to perform, and adsorbed triazines are stable for up to three months.

VOLUME II

SESSION D

ANALYTICAL METHODS RESEARCH

POSTER PRESENTATIONS

DP1

ROBUSTNESS OF THE STUDENT'S T TEST WITH CENSORED ENVIRONMENTAL QUALITY DATA

E.E Creese*

Creese Environmental Consulting,
P.O. Box 91, Waterloo, Ontario
N2J 3Z6

Introduction

A data set with observations below a certain cut-off point, for example, an analytical detection limit, is termed *censored*. The log-regression approach was followed here in determining means and standard deviations of censored data sets to be used in the Student's t test. Of course, this would result in unjustifiably low type I error rates (α). The goal of this project was to ascertain, by Monte Carlo methods, what the real values of α were.

Previous studies (Gilliom & Helsel, 1986; Helsel & Gilliom, 1986) have shown that, of the methods that they investigated, log-probability regression to the curve of a normal distribution was the most robust for estimating population parameters such as the mean and standard deviation of parent populations of environmental data. This project took as a starting point the assumption that the log-normal distribution is the most likely parent distribution of chemical water quality data. It endeavored to assess the reliability of simple hypothesis testing, such as the t test, when population or sample parameters are estimated by log-probability regression.

The basic procedure was to generate a large number of simulated samples, all with a specified number of observations. Then censoring was performed at a certain defined cut-off points. Two types of censoring have been designated (David, 1981). In type I censoring, all data below a fixed value are eliminated. This is the type of censoring observed by environmental scientists. The 'fixed value' is the concentration of a particular chemical in an environmental medium below which it can not be detected by the available analytical methods, in other words, the detection limit of the chemical. In contrast, type II censoring eliminates values so that a fixed proportion of the data remain.

The mean and variance of the population (or sample, depending on the method) were estimated by log-probability regression. Then, hypothesis tests were performed using the estimated mean and variance to determine if the sample mean could be inferred to be equal to the population mean. Since, the population mean was known, which, of course, was the whole point of using simulated data, one could say whether or not the statistical test failed. Such a failure, that of rejecting a true null hypothesis, is termed a type I error. This work involved the use of Monte Carlo methods to compare nominal type I error rates to actual type I error rates.

One regression method was chosen and used to calculate data for 'error tables'. Knowing the number of observations in a sample set, the number of observations

below the detection limit and the nominal type I error rate, error tables would be used by environmental scientists to determine the actual type I error rate of a t test.

Methods

Hardware, Software, Quality Control

The hardware and software used in this project have already been described (Creese, 1988). Also described were the methods used for generating random samples with log-normal distribution and details of quality control measures.

Censoring

Initially, type I censoring was employed, as described in Creese (1988). Although type I censoring is what is encountered by environmental scientists, difficulties were foreseen with using error tables set up by this method. After performing the regression, one would calculate the proportion of one's sample that was censored. It would be very unlikely that this proportion would correspond exactly to a proportion chosen in prepared tables. Interpolation between tables would therefore be required. Interpolation is unnecessary with table set up by type II censoring. Therefore, part way through this project, a switch was made to type II censoring.

Simulation Runs

The method of performing z tests was described in Creese (1988). The perfomance of t tests was carried out in a similar manner. Values of the inverse t cumulative probability functions were calculated by numerical integration of the following expression:

$$p_i = C \int_{-\infty}^{t_i} (1 + t^2 / df) \exp [\, 2 / (df + 1) \,] \, dt$$

where C is:

$$C = (\pi \, df)^{-0.5} (\Gamma [\, (df + 1) / 2] / \Gamma [\, df / 2 \,])$$

Results

Methods of Regression

The first method used was type I censoring with hypothesis testing by z test, using, n, the sample size before censoring. A confidence interval for the appropriate probability, p, was constructed about the estimate of population mean, thus:

$$m_y \pm z [p] \, s_y / \sqrt{n} \quad | \, p = 1 - \alpha / 2$$

A type I error is indicated if the true population mean, μ_y, falls outside the confidence interval. This method of determining actual type I error rates is designated here as Method 1. Method 2 was almost identical to Method 1 except that in the above expression for the confidence interval, n was set equal to n_D, the number of observations remaining after censoring. Method 3 was that same as Method 1 except that a t regression was used. Method 4 agreed with Method 2 in using n_D for calculating the confidence intervals, but differed from the other three methods in using type II censoring. Table 1 summarizes these methods.

Table 1. Summary of methods of regression used. Sample size used refers to the sample size used in calculating the confidence intervals for hypothesis testing.

Method	Censoring	Test	Sample size used
1	type I	z	n
2	type I	z	n_D
3	type I	t	n
4	type II	t	n_D

Table 2 contains comparisons of three of these methods. Method 4 gave the lowest actual type I error rates of any of the four methods.

Table 2. Comparison of Methods 1, 3 and 4 with sample number n = 5. The nominal type I error rate is 5%. n_D is the number of observations above detection, a is the actual type I error rate, and r is the number of regressions actually performed.

Method	Censoring	n_D	r	a
1	0%	various	1000	6.7%
1	20%	various	985	7.9%
1	40%	various	904	12.5%
1	60%	various	669	27.4%
1	80%	various	279	51.3%
3	0%	various	1000	3.8%
3	20%	various	985	5.6%
3	40%	various	904	13.6%
3	60%	various	669	39.0%
3	80%	various	279	65.6%
4	type II	5	1000	3.8%
4	type II	4	1000	3.6%
4	type II	3	1000	5.0%
4	type II	2	1000	9.7%

It was found that coefficient of variance, cv, did not significantly affect the values of a generated by log regression on the Student's t variable.

Error tables were generated for nominal type I error rates of 5% and 1%. These are Tables 3 and 4.

Discussion

Several methods were tried and one was chosen for the development of error tables. A method was chosen which incorporates type II censoring and regression on Student's t functions. The use of type II censoring makes the error tables much easier to use, since no interpolation is necessary. The t regression also gives the lowest actual type I error rates of any of the methods tried. It unfortunately also produces wider confidence limits. Having lower actual α is still an advantage, however, in that the experimenter has the option of reducing the size of the confidence limits by increasing the sample size. Using the chosen method, the t-test was found to be quite robust, if the degree of censoring was not too severe. With a sample size of 10 and 5

observations below the detection limit, a nominal α of 5% is really approximately 6%, and a nominal α of 1% is really about 2%. But with 8 observations below the detection limit, a nominal α of 5% becomes a real α of 26%, and a nominal α of 1% becomes a real α of 6%.

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Table 3. Actual type I error rate, a, given as a percentage. Nominal type I error rate: α = 5.0%.

n \ n_D	2	3	4	5	6	7	8	9	10
3	5.8	4.1	.	.	.	.	.	.	.
4	7.6	3.9	3.6	.	.	.	.	.	.
5	9.7	5.0	3.6	3.8	.	.	.	.	.
6	11.8	6.1	4.8	3.9	3.4	.	.	.	.
7	16.0	9.3	6.2	4.2	4.3	4.4	.	.	.
8	21.7	13.0	7.4	3.6	3.2	3.2	3.0	.	.
9	23.6	14.1	8.4	5.3	3.8	3.6	4.4	4.0	.
10	26.2	15.8	10.1	5.9	4.8	4.0	3.9	3.9	4.1

Table 4. Actual type I error rate, a, given as a percentage. Nominal type I error rate: α = 1.0%.

n \ n_D	2	3	4	5	6	7	8	9	10
3	0.6	0.9	.	.	.	.	.	.	.
4	1.2	0.7	0.3	.	.	.	.	.	.
5	1.6	0.9	0.9	0.9	.	.	.	.	.
6	2.0	1.4	0.7	0.8	0.9	.	.	.	.
7	3.4	1.8	1.4	1.1	1.2	0.9	.	.	.
8	4.2	3.1	2.0	1.0	0.5	0.3	0.2	.	.
9	5.2	3.4	2.7	1.3	1.0	1.2	0.9	0.6	.
10	6.1	4.3	2.9	1.7	1.1	1.0	0.9	1.2	1.0

DP2

DEVELOPMENT OF STANDARD METHODOLOGY FOR THE EVALUATION OF ORGANIC CONTAMINANTS LEACHING FROM MUNICIPAL AND INDUSTRIAL WASTES

V. Breitung, F.W. Karasek
Department of Chemistry, University of Waterloo
Waterloo, Ontario, Canada, N2L 3G1

ABSTRACT

At this time the Ontario Ministry of the Environment, Toronto, has only a method for the evaluation of leaching of inorganic species. There is no such method for organic compounds. The method described here for a standard leaching procedure consists of a simple elution with water of fly ash packed in a stainless steel column using an HPLC pump, followed by passage through an organic solvent layer as an on-line partitioning step for organics. A semipreparative HPLC was used to fractionate the organic concentrate into several classes of compounds. Gas chromatography/ mass spectrometry using various ionization modes was used to identify the compounds in each fraction. A quantitation of the major compounds found in the leachates is provided. The basic analytical procedure described in this study can be used as a rapid method for determination of the extent of potential leaching from waste samples.

INTRODUCTION

Many household products contain hazardous chemicals, some of which will ultimately find their way into municipal landfills. In addition, the final depository for most of the products of our modern industrial society is the municipal waste landfill, where waste compounds dissolve and degrade in the anaerobic environment, releasing possibly toxic degradation products. Since municipal and industrial landfills are numerous and contain many of the same compounds as found in industrial wastes, it is essential to evaluate the risk to human health and the environment from exposure to groundwater contaminated with municipal waste landfill leachate.

Data has been presented on the quality of leachate, surface water, ground water and air (1). Based on these data there is a potential threat of groundwater pollution and therefore to human health. In this study fly ash is used as a waste sample, because it is representative of material containing hazardous compounds and is relatively easy to handle. More than 600 organic compounds have been identified in fly ash (2), some highly toxic. The fly ash, placed in a column, is extracted with water pumped through, simulating the events occurring in a landfill site. A one-step fractionation procedure using normal phase HPLC with gradient elution is performed as modified from a method described by Tong (3), followed by concentration and GC or GC/MS analysis. The methodology developed is representative of naturally occurring leaching processes and is also applicable to laboratory studies of a wide variety of waste.

EXPERIMENTAL SECTION

A stainless steel column (35 cm x 1.5 cm i.d.) with commercial HPLC fritts at the ends was wet filled with fly ash (15 g) and connected to an HPLC pump (Varian 5000 liquid chromatograph and Mandel piston pump Model 302, respectively). The column was eluted with 1.5 L of water at 1.0 ml/min (typical groundwater flow reaches from 15 ml/h to 60 ml/h and 1.75 m/d to 6.98 m/d respectively) (5). The eluent passed (i) through a toluene (BDH Omnisolv) layer in a chromatographic column (30 cm = 250 ml toluene), (ii) through a stirred dichloromethane (DCM, BDH Omnisolv) layer of 500 ml. In a long term experiment 10 L water was passed through the fly ash column and the DCM layer was replaced every 24 h. The combined solvent extracts were concentrated and brought into toluene for GC analysis and HPLC separation. Seven fly ash extractions were carried out using the same method, to test the reproducibility of the method. The collected extracts were used for the quantitation studies as well.

All separations were done using a Varian 5000 liquid chromatograph with UV detection at 254 nm. The samples were injected through a 100 microliter loop onto a normal phase silica column and eluted by a gradient program with hexane and DCM. Three fractions were collected from 0-10 minutes, 10-15 minutes, and 15-75 minutes. The HPLC fractions were concentrated and analyzed by gas chromatography with flame ionization and electron

capture detection (HP 5880A GC equipped with a J & W 30m x 0.32mm i.d. DB-5 fused silica column), and by gas chromatography with mass spectrometer detection (both an HP5970 GC/MSD (electron impact ionization (EI) and selected ion monitoring) and an HP5987A GC/MS (in EI and positive chemical ionization mode).

RESULTS AND DISCUSSION

The methodology developed is shown in Figure 1. Following the HPLC extraction with water, the eluent is pumped into the stirred DCM layer (maximizing contact between phases) in a round bottom flask. The extraction efficiency using DCM as an adsorbent is 90-98.9 % for chlorinated compounds but only 55-64.4 % for hydrocarbons. Clean-up and preseparation into three classes of compounds is accomplished using HPLC. Figures 2 and 3 show GC traces of the water extract obtained using GC/FID and GC/ECD after the separation step. The compounds identified in the water extracts are shown in Table 1. Quantitation of the compounds using an external standard was performed only for the major compounds found in the leachates using GC/MS/SCAN (hydrocarbons) and GC/MS/SIM (chlorinated organics). The results are shown in Table 2.

The methodology developed shows reproducibility for trace amounts of compounds. Standard deviations of 5-8 %, 16-19 % and 30.8-37.8% were obtained for hydrocarbons, chlorinated benzenes and chlorinated phenols, respectively.

The data from this study indicates that water is able to dissolve hazardous compounds out of the waste matrix. The fact that impure water contacts the fly ash/waste during the formation of a leachate increases the possibility of groundwater pollution drastically. It is well known that organic solvents in water have a cosolvent effect for other organic compounds and increase the solubility of hazardous organic compounds (7).

CONCLUSIONS AND RECOMMENDATIONS

In this study a simple methodology is described for evaluation of organic contaminants. The method developed shows reproducibility and is representative of leaching of organic compounds out of fly ash. This method is also applicable to different kinds of homogenized waste samples. To identify more compounds it is recommended to increase the amount of fly ash or waste and to treat the organic extract with aqueous acid and base solution to separate acid, base and neutral compounds. To receive information about the yield of the water extraction/recovery rate it will be useful to work with ^{13}C-labelled chlorinated compounds as internal standards under identical conditions.

The developed method can easily be varied in laboratory usage. With more representative solvents (different dissolved oxygen content content or surfactant agents) and different pH-values the results obtained are closer to naturally occurring processes. With this kind of information one should be able to estimate the risk for groundwater pollution and human health caused by hazardous waste in landfill sites.

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Table 1 Compounds identified in water extractions

Compound	ID-Method	Compound	ID-Method
HPLC Fraction #1			
hexadecane	1,2,3	tetratriacontane	1,2,3
heptadecane	1,2,3	pentatriacontane	1,2,3
octadecane	1,2,3	hexatriacontane	1,2,3
nonadecane	1,2,3	heptatriacontane	1,2,3
eicosane	1,2,3	octatriacontane	1,2,3
heneicosane	1,2,3		
docosane	1,2,3	1,3,5 trichlorobenzene	
tricosane	1,2,3	1,2,3,4 tetrachlorobenzene	1,2
tetracosane	1,2,3	pentachlorobenzene	1,2
pentacosane	1,2,3	hexachlorobenzene	1,2
hexacosane	1,2,3		
heptacosane	1,2,3	**HPLC Fraction #2**	
octacosane	1,2,3		
nonacosane	1,2,3	2,4,5 trichlorophenol	
triacontane	1,2,3	3,4,5 trichlorophenol	1,2
hentriacontane	1,2,3	2,3,4,5 tetrachlorophenol	1,2
dotriacontane	1,2,3	2,3,5,6 tetrachlorophenol	1,2
tritriacontan	1,2,3	pentachlorophenol	1,2
HPLC Fraction #3			
benzaldehyde 4-hydroxy-3-methoxy			2,3
1,2 benzene dicarboxylicacid diethylether			2,3
hexanedioicacid dibutylester			2,3
1,2 benzene dicarboxylicacid dibutylester			2,3
benzene,1-methoxy-4-phenoxy			2,3
hexanoicacid 1-methylethylester			2,3
9-octadecen-1-ol			2,3
benzenebutaneamine			2,3
1,2 benzene dicarboxylicacid dicyclohexylester			2,3
1,2 benzene dicarboxylicacid bis(2-ethylhexyl)ester			2,3

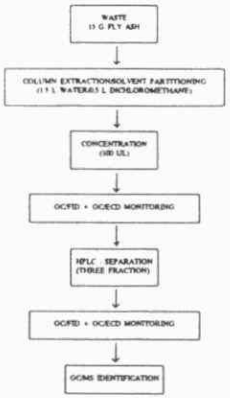
1=retention time standard
2=Probability Based Matching (PBM) (GC/MS-EI)
3=molecular weight (GC/MS-PCI)

NC = not confirmed
(+) = not possible to quantify, but present

Table 2 Quantitation of compounds in the leachate obtained with the column elution method [concentration in ug/l leachate (ppb)]

Compound		Compound	
docosane	0.030	tetratriacontane	0.192
tricosane	0.064	pentatriacontane	0.160
tetracosane	0.096	hexatriacontane	0.094
pentacosane	0.200	heptatriacontane	0.053
hexacosane	0.186	octatriacontane	(+)
heptacosane	0.208	trichlorobenzene	0.290
octacosane	NA	tetrachlorobenzene	1.240
nonacosane	0.200	pentachlorobenzene	0.750
triacontane	0.239	hexachlorobenzene	0.270
hentriacontane	0.182	trichlorophenol	0.120
dotriacontane	0.160	tetrachlorophenol	0.230
tritriacontane	0.178	pentachlorophenol	5.740

Figure 1 Leaching methodology developed



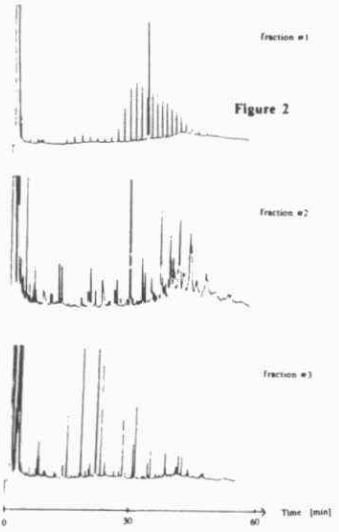


Figure 2

GC/FID chromatograms obtained after HPLC-separation

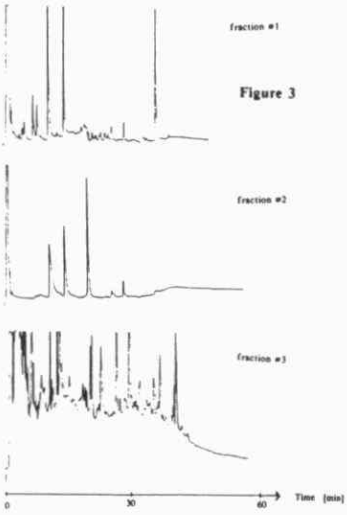


Figure 3

GC/ECD chromatograms obtained after HPLC-separation

DP3

A METHOD FOR ULTRA TRACE METAL DETERMINATION IN ACID PRECIPITATION SAMPLES USING HIGH PERFORMANCE ION CHROMATOGRAPHY AND INDUCTIVELY COUPLED PLASMA SOURCE MASS SPECTROMETRY

M.J. Powell*, J. Hipfner and D.W. Boomer, Inorganic Trace Contaminants Section, Laboratory Services Branch, Ministry of the Environment, Rexdale, Ontario M9W 5L1.

Environmental scientists studying the affects of acid precipitation on lakes and streams need reliable information on the elemental concentrations in different sample matrices. For example, trace elements such as cadmium and lead can be toxic to aquatic life at concentrations in the nanogram per litre range and may act synergistically with other components of acid rain to further the detriment of the environment (1). Consequently, reliable analytical methods to detect and quantify ultra low-level trace elements are needed to map affected regions and to support studies of toxicity at low concerntrations. Few conventional analytical instruments can obtain the detection limits for analytes required in some of these studies. However, instrument performance can be dramatically improved through sample preconcentration.

The conventional method of preconcentration involves quantitative transfer and overnight evaporation. This method is labour intensive, time consuming and can introduce inaccuracies caused by contamination. To minimize these errors, an automated technique has been developed to preconcentrate samples in a closed system using a high performance ion chromatograph (HPIC). A commercially available cation exchange column (2) is used for the preconcentration. The mobile phase is delivered to the column using a high pressure pump and valve system. Depending on the preconcentration factor required, a known volume of sample is deposited on the column. The analytes are then eluted from the column using a relatively strong acid. The preconcentrated "plug" or solution is then introduced into an inductively coupled plasma mass spectrometer (ICP-MS) to determine analyte concentration. The advantage of using an ICP-MS is the high sensitivity and a very fast sequential scanning ability. These capabilities further enhance the preconcentration step to obtain both ultra low detection limits and rapid multielement analysis.

In the method development, optimization of the HPIC to the ICP-MS was necessary to obtain peak performance. Parameters that were investigated were column capacity, variations in concentration and flowrate of two different eluents (nitric and hydrochloric acids), and effects of varying sample pH. The optimum conditions for the above parameters were obtained experimentally. The most favorable settings to produce well defined narrow analyte peak widths were used since the ICP-MS uses peak height measurements for concentration calculations.

Column Capacity. Column capacity was determined experimentally by monitoring the analyte signal of a known standard in the mobile phase as it emerged from the column. Breakthrough was indicated when the continuously monitored signal increased significantly above the background signal. The column capacity was determined to be in the order of 6 micro-equivalents for each element studied.

Effects of Eluent Strength on Retention Time. Experimental results show that the removal of cations from the column is dependent on the acidic strength. In general, the higher the acid concentration of the eluent, the shorter the retention time. A series of experiments were conducted with nitric and hydrochloric acids. Nitric acid at a concentration of 5% was the optimum eluent.

Flowrate. Effects of flowrate on retention time were determined by monitoring elution profiles of analytes while changing the flowrate of the eluent. Experimental results showed that as the flowrate increases, the retention time decreases. The optimum flowrate obtained was 3.5 ml/min.

Effects of Sample pH. Samples submitted to our laboratory may vary in pH, and any analaytical method chosen for sample analysis must ensure that variations in sample pH will not bias the accuracy of the results. Experimental results show that varying the pH range of a sample from 1.6 to 9.5 did not adversely affect HPIC-ICP-MS response. Therefore bias in the results will not take place and samples need not be adjusted in this range.

Copper, cadmium and lead were chosen as test analytes because of their significance in many environmental studies. They are also representative of the mass range that is most frequently scanned. The HPIC-ICP-MS detection limits for these elements are in the sub - nanogram per litre range.

During the initial method development stages, the HPIC was interfaced directly with the ICP-MS for ease of experimental study. To preconcentrate a sample to gain reasonable detection limits, a significant volume of sample must be loaded onto the column. If more than one sample is to be analysed, this could be a lengthy procedure. In order to reduce to length of analysis time and to allow the ICP-MS to be used for other tasks, the HPIC has been automated to run "off-line" from the ICP-MS.

The "off-line" HPIC technique has reduced operating cost and freed personnel for other duties. A Zymark robot arm is used to sample from up to 24 sample containers of 100 mL each. The sample is then introduced to the HPIC and the fraction is collected by an ISCO auto-sampler configured as a fraction collector. The Zymark computer controls the robot arm, the switching of the electrically actuated rotary valves in the HPIC system and the sequences for the fraction collector. This automated technique can be run overnight and unattended.

Experimental results show that the method is accurate in the determination of trace metal concentrations in acid precipitation. However, with a different matrix such as surface water and depending on the geographic location of the sample sites, uncertainties in accuracy can be expected with increasing concentration levels of major elements such as Ca and Mg. Investigations in modifications to the chromatographic procedure to reduce these effects will be conducted in the future.

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DP4

POSTER PRESENTATION

EXTRACTION AND CONCENTRATION METHOD FOR TESTING OF LANDFILL LEACHATES

BY

JACK BRADY, ART HORTON, TIM HARRISON, JUDITH BEETHAM, KAY SHAW, GORDON THOMAS

ORTECH International, Mississauga, Ontario

Introduction

There is a need for the development and validation of test protocols to assess the degree of leachability and mobility of potentially hazardous materials contained in landfill disposal sites. A detailed chemical analysis and identification of all chemical species in leachates and groundwater is desirable, but such survey type analyses are time consuming.

Short-term biological tests are attracting interest as a basis for possible regulatory purposes. The reason is that these tests provide some predictive value regarding health effects. The overall goal of this program is to develop and validate concentration methods for organic chemicals from groundwater for use with the Ames bioassay.

SELECTION OF CHEMICALS

Initially, it was necessary to select a limited number of chemical compounds for inclusion in an aqueous solution ("cocktail mix"), in order to permit the validation of isolation/concentration techniques and measurement methods of the concentrates. The guidelines used for selecting the reference compounds were:

- to provide a wide selection of functional groups
- to represent, where possible, a range of pertinent physical properties such as volatility and polarity
- to choose, where possible, known water pollutants
- to select, when possible, halogenated derivatives of several parent compounds
- resistance to degradation
- to include known mutagenic compounds

This presentation deals mainly with the selected volatile compounds The compounds selected are listed in Table I.

CHEMICAL TESTING

Preliminary chemical data was obtained by direct injection of suitable aliquots (1-3μL) of the individual compounds initially, and then of a combined mixture of the compounds into a gas chromatograph/mass spectrometric (GC/MS) system. The system used was a HP Model 5890A series capillary GC with an HP 5970A Mass Selective Detector. The data system was an HP ChemStation with an HP 9816S computer and HP 9133XV disc drive printer.

Data was obtained for all the compounds using both total scan and selected ion monitoring procedures. Either or both methods were used for identification and quantification during the validation of purging concentration techniques for recovery of the target chemicals from goundwater. In Table I, the compounds are listed together with their respective retention times and the major ions (m/e) present in their mass spectra.

CONCENTRATION METHODS

Solutions of the selected chemicals at 20μg/L concentrations were prepared in a large scale purging and trapping apparatus (20 L).

This paper will present an evaluation of the effect of parameters such as water volume, water temperature, purge flow rates, purge times on the recovery of target compounds with the use of a cryogenic trapping device. Transfer of the trapped compounds into a solvent compatible with the Ames bioassay will be addressed.

TABLE I

GAS CHROMATOGRAPHIC AND MASS SPECTRAL DATA FOR CHEMICALS IN "COCKTAIL MIX"

Compound	Retention Time (min)	Base Peak in Mass Spectrum (m/e)
1,1-dichloroethylene	3.27	61
1,2-dichloropropane	6.57	63
Methyl isobutyl ketone	7.69	43
1,2-dibromoethane*	9.26	107
o-xylene	11.05	91

* known mutagen

DP5

SOLID PHASE EXTRACTION OF POLYAROMATIC HYDROCARBONS FROM DRINKING WATER.

W.G. Craig, J.M. Craig, and R.G.Walker, Paracel Laboratories Ltd., Nepean, Ontario, K2G OG3 and C.D. Hall, Laboratory Services Branch, Environment Ontario, Rexdale, ON, M9W 5L1.

The use of solid phase extraction (SPE) for the analysis of polyaromatic hydrocarbons in water has been investigated. Current methodology involves the liquid liquid extraction (LLE) of the PAHs using dichloromethane followed by quantitation by HPLC with fluorescent detection. This research project was undertaken in order to develop a method that would allow the simplification of existing techniques, reduced use of toxic solvents, greater reproducibility, increased operator throughput, decreased storage and shipping costs, and that would be more amenable to the introduction of robotics.

The study began with the examination of phenyl, cyclohexyl, octadecyl and cyanopropyl phases using ethyl acetate and iso-octane as the eluting solvent. All phases were acceptable (but for convenience the octadecyl phase was selected for detailed examination) and iso-octane was the better eluting solvent.

Products from five different manufacturers (Baker, Supelco, Analytichem, Alltech and Waters) were evaluated and found to be comparable. Five different Lot Numbers from one manufacturer (J. T. Baker) were examined and all lots were found to give acceptable results.

The recoveries were found to be consistent over a twenty fold range of concentrations, e.g., from 125 to 2500 ng/L in the case of pyrene.

PAHs were shown to be stable, when adsorbed onto octadecyl SPE columns, by storing columns with adsorbed analytes for periods of up to three months at room temperature.

The recoveries of PAHs from four different natural waters (Verner raw water, Lakeview raw water, Ottawa City tap water and a drilled rural well) and one reference water (supplied by Dr. Brian Hollebone of Carleton University) were determined. It was found that with a matrix other than tap water the recoveries were very low, <20% in some cases, when iso-octane is used as the eluting solvent. The poor recoveries were likely caused by the multitude of phases present, preventing the interaction between iso-octane and adsorbed analytes. This situation was easily corrected by eluting, first, with a small volume of acetonitrile followed with iso-octane. The acetonitrile replaced the water and, being miscible with both water and iso-octane, allowed a more efficient elution.

In order to simplify the method, the effect of alternative eluting solvents were ascertained. Ten ml of iso-octane were required for complete elution of analytes from 500 mg columns and the solvent then had to be evaporated prior to quantitation. Acetonitrile (3 mL) and, alternatively, toluene (3 mL) were used to elute adsorbed analytes, followed by direct injection of the eluate onto the HPLC. Recoveries were low for the higher molecular weight compounds when acetonitrile was used and low for the low molecular weight compounds when toluene was used. Replacement of iso-octane with pentane, which is more easily volatilized, gave excellent recoveries for all the PAHs including naphthalene.

Interfering substances were not a problem, throughout the project, when quantitation was by HPLC with a fluorescent detector.

Breakthrough Volumes:

The possibility that adsorbed analytes might be desorbed form the column during passage of the sample was investigated by adsorbing small amounts of a PAH (e.g., 10 ug of anthracene) onto a 500 mg octadecyl column, pumping 1940 ml of water through the column at a flow rate of 5 ml/min using an HPLC, and monitoring the passed water with a fluorescent detector. Under these conditions breakthrough would have easily been seen at the 10 ng/mL (10 ug/L) level in the passed water and no evidence of anthracene in the passed water was found. Thus, we can conclude that, for this quantity of anthracene, even after the passage of more than twice the amount of water present in one sample (800 ml), that breakthrough, if it occurs, is less than one thousandth of the quantity of adsorbed analyte per mL of passed water. Similar results were obtained for fluoranthene.

Conclusions:

The use of solid phase extraction for the analysis of PAHs in water is a feasible analytical technique allowing the quantitation of PAHs including naphthalene from drinking water. Neither breakthrough of analytes, nor interferences when using HPLC with fluorescent detection, are a problem with the methodology developed. Further research should include work to further simplify the elution process. Approaches might include:

1) the use of 200 mg columns (which have a smaller bed volume thereby allowing complete elution with a smaller volume of solvent than the 500 mg size), elution with acetonitrile, followed by direct injection, or

2) replacement of the highly retentive C-18 phase with C-8 or C-2, or another less retentive phase to allow direct acetonitrile elution.

DP6

ADAPTATION OF WATER PRECONCENTRATION TECHNIQUES DEVELOPED FOR PCDD ANALYSIS TO OTHER TARGET ORGANIC POLLUTANTS.

C.S. Shewchuk*, L.J. Brownlee and B.R. Hollebone, Chemistry Department, Carleton University, Ottawa, Ontario, K1S 5B6.

INTRODUCTION

These laboratories, in conjunction with the Ontario Ministry of Environment, have developed a sampling unit capable of preconcentrating water for ultratrace detection of PCDDs as part of a water quality monitoring program for raw and treated drinking water[1].

The automated preconcentration sampler (APS) is able to accept treated or raw water sources. A schematic of the sampler operation is shown in figure 1. The analytical process in the sampler system provides a dual function; first to filter particulate from the sampler stream and then to concentrate the remaining water soluble target organics on the adsorption column for subsequent analysis. The adsorption technology utilizes a macroreticular resin (XAD-2) for which sampling conditions and elution and detection procedures have been established to permit recovery and analysis of dioxins at the ppq level[2]. The filter system is based on setting the distinction between dissolved and insoluble particles at 0.45 um. The duplicate analytical systems each consist of 2 tubular filters placed in series to accommodate 100 L of 50 NTU water and trapping >0.3 um particles at 98% retention.

Natural water contains suspended mineral particles coated with colloidal metal oxides and humic acids. These adsorb and transport significant amounts of organic contaminants. This interferes with the accurate recovery and quantitation of these compounds since the natural compounds compete successfully with conventional analytical adsorption media. The APS overcomes this loss factor by preconcentrating organics using analytical filtration and resin technology in series.

Depending on the specific particulates in a natural water supply, organic pollutants will establish an equilibrium of dissolved and adsorbed forms. The understanding of the influence the particulate and water matrices have in the distribution equilibrium between the filtered precipitates and the adsorbed solubles. This influence will vary with the molecular weight, aromaticity and chlorination of the pollutant. This knowledge is necessary for transfer of this technology to a more comprehensive protocol for the APS unit. The behaviour of eight compounds selected from the Ontario Ministry of the Environment priority pollutant list have been studied in the presence of a representative clay suspension using the APS sampler.

EXPERIMENTAL

The compounds chosen for this study include two polyaromatic hydrocarbons, benzoperylene and anthracene, and five organochlorines, PCB's, trichlorobenzene, octachlorostyrene, trichlorotoluene, lindane and mirex. These compounds vary in aromaticity, molecular weight, and degree of chlorination. Initial experiments were performed to determine the distribution of the target organics in an experimental situation by measuring the concentration of organics located in the water, on the particles, or bound to the glass, as a function of turbidity over a fixed time period.

Illite solutions with turbidities of 0, 0.1, 0.5, 1.0, 5.0 and 10.0 NTU were spiked at a concentration of 10 ng/L with the standard mixture of target organics and equilibrated for 3 days. The samples were then filtered through a glass fiber filter of 0.5 um nominal pore size. The analytes were removed from the filter/particulate by soxhlet extraction with acetone/hexane, from the water with hexane, and from the flask with acetone/hexane. They

ACF = ACTIVATED CHARCOAL FILTER
AR = AIR BUBBLE REMOVER
CV = CHECK VALVE (1PSI)
COL = COLUMN
D = 3 WAY DIVERTER
F = FILTERS
FM = VARIABLE AREA FLOW METER
MFS = MICRO FLOW SENSOR
MIX = MIXING TUBE
NCV = NORM CLOSED VALVE
P = PRESSURE GAUGE
PS = PRESSURE SWITCH
PUM = MICRO PUMP
RES = RESERVOIR RAW WATER
SP = SPIKE PUMP
SPIKE RES = SPIKE RESERVOIR

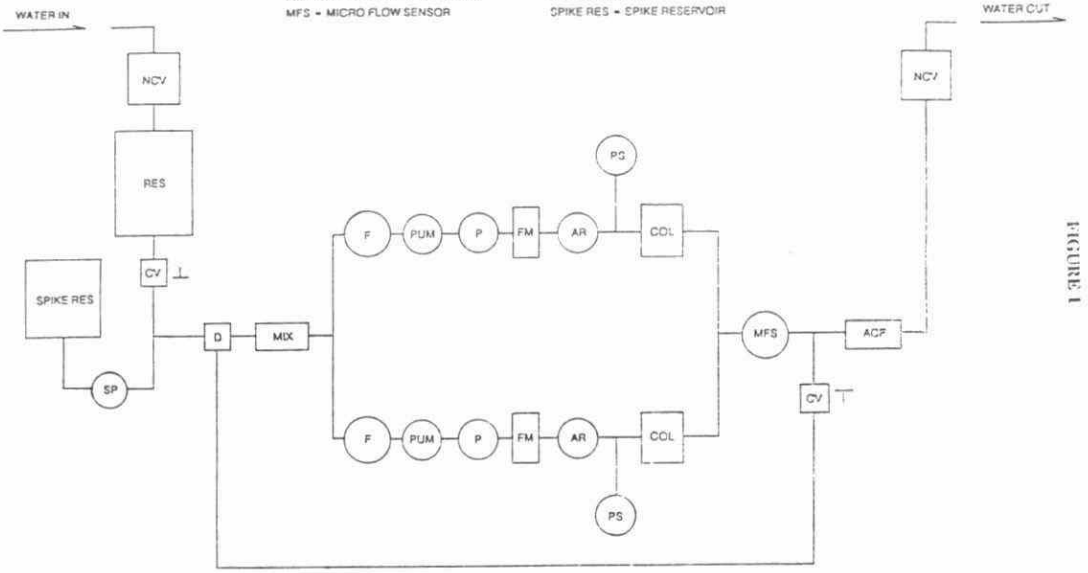

FIGURE 1

FLOW CHART
APS-MKII O/M

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were cleaned up using Florisil and will be analyzed by GC/ECD and GC/MS.

The following set of experiments are in progress:

APS Testing

The distribution of target organics between filters and XAD resin in the APS sampler will be studied as a function of turbidity. Distilled water spiked with a standard mixture of target organics in methanol and varying concentration of illite will be run through the sampler. 20 L of water per side, for a total of 40 L will be sampled in each run.

The first run has been completed and consists of distilled water only, passed through filters and columns, to observe background noise. Then, preliminary tests will be performed to indicate adsorbance preferences of the trace organics. These will consist of the standard spiking mixture and distilled water passed through the column only, then, in another run, passed through the filters and columns. Experiments will then be done by passing illite solutions at turbidities of 0.1, 0.5, 1.0, 5.0 and 10.0 NTU through the filters and columns. This selection of turbidities was chosen because it represents turbidities found regularly in treated and surface waters[3] and are within the limitations of filter capacity of the Balston tubular filters.

Once the results from the target distribution experiments are known, the tests may be repeated with tap water and Mer Bleu bog water. These matrices will give us an indication of how different water sources affect particulate distribution.

Note:
All distilled water used in this study is filtered through a Millipore system and subsequently passed through an XAD-2 column.

The sampler is designed to run samples in duplicate (one sample per side) and each side consists of two filters placed in series (2 um and 0.3 um respectively) and an XAD-2 resin column.

The XAD-2 resin was used for the selected compounds since it has been successfully used in the determination of organochlorines from water[4].

***In situ* Extraction Apparatus**

The current procedure for extraction of organic analytes from a solid matrix such as a filter or soil sample is soxhlet extraction.

To adapt this process to Balston or cartridge filters there are several problems. To accommodate the filter size, a soxhlet apparatus must have a sample chamber of 1500 mL or 5000 mL. An apparatus of this size is awkward to clean and handle on a routine basis. In addition, in order to use a traditional Soxhlet apparatus, the filter must be transferred from the filter housing to the apparatus without compromising the analytical integrity of the filter or contaminating the worker by exposure to toxic chemicals on the filter.

The objective of this part of the study is examine the feasibility of an *in situ* Soxhlet extractor using the filter housing as the sampler compartment of the extraction vessel.

The apparatus is completed and is ready for testing.

The new apparatus (figures 2 and 3) consists of:

(i) Balston stainless steel filter holder.

(ii) A 2000 mL, two necked round bottom flask. The center neck is straight, the side neck is angled. Both necks have 24/40 ground glass joints.

(iii) A permanent syphon/condenser system that is mounted to a wall rack. The condenser is a copper coil slightly wider in diameter then the filter housing that will also function as the housing mount. The condenser is attached to an aluminum back by Swagelok bulkhead connectors at the water inlet and outlet. For more efficient cooling an insulating material is wrapped around the outside of the coil. The drain port at the bottom of the filter housing acts as the port for the 1/4" stainless steel syphon arm. It is attached to the bottom panel of the unit with a bulkhead connector at points A and B. A 1/2" glass/metal transition tube connects the syphon arm to the center neck of the round bottom flask containing the solvent via a 24/40 ground glass joint. The bulkhead connector serves as the transition point between the two tubing sizes.

(iv) A vapour inlet connects the angled neck of the round bottom flask with the water out port on the filter housing. A 1/2" stainless steel tube is connected to the housing by a Swagelok adapter. A flexible stainless steel/glass end transition tube connects the vapour arm with the round bottom flask via a 24/40 ground glass joint.

RESULTS AND DISCUSSION:

The data from the study will be presented as a result of increasing complexity of the matrix; distilled water, distilled water with varying concentrations of illite, tap water, and bog water.

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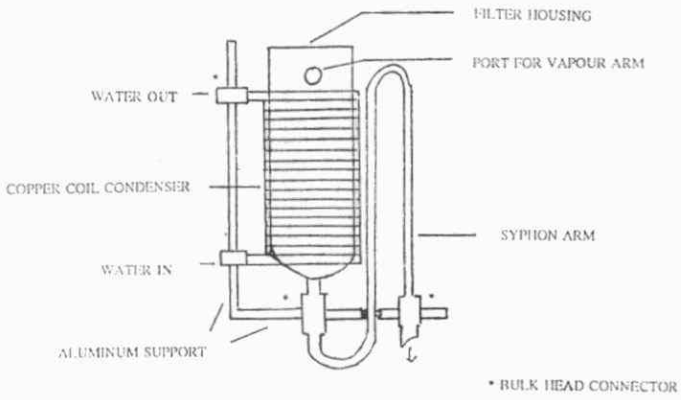
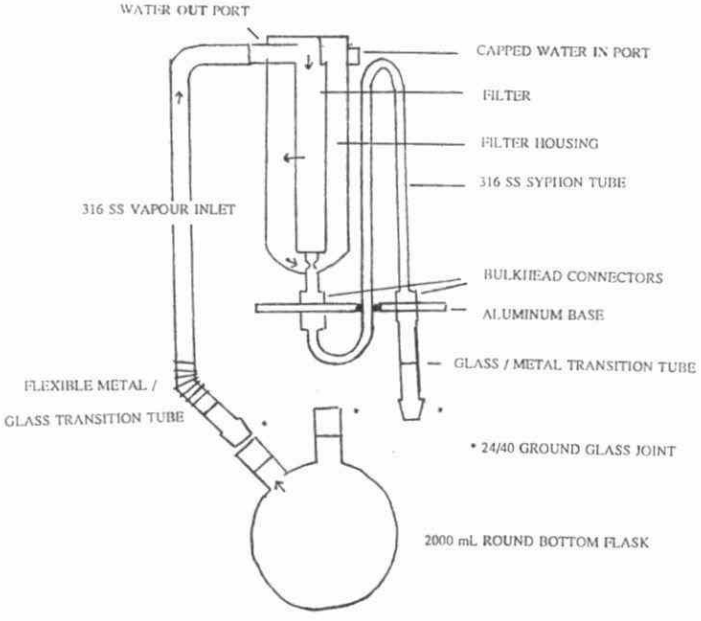
FIGURE 2: *IN SITU* APPARATUS: CONDENSER/SYPHON ASSEMBLY



NOTE: SYPHON ARM AND VAPOUR ARM ARE AT 90°

FIGURE 3: *IN SITU* APPARATUS: TOTAL APPARATUS



NOTE: SYPHON ARM AND VAPOUR ARM ARE AT 90°

DP7

ADAPTATION OF WATER PRECONCENTRATION TECHNIQUES FOR TRACE METAL DETECTION. B.R. Hollebone, E. Dowdall, K.L. Singfield, Department of Chemistry, Carleton University, Ottawa, Ontario, K1S 5B6; F. Hopper, Laboratory Services Branch, MOE.

Introduction

The overall goal of this project is the design, construction and verification of a water sampler for the preconcentration of trace metals from raw and treated drinking water, in preparation for analysis by inductively coupled plasma emission spectroscopy (ICPES). This has been approached through the adaptation of an existing preconcentration system for organic pollutants in raw and treated water developed in these laboratories, and currently under test by the Ministry of the Environment. A schematic of the water sampler is shown in figure 1.

To use ICPES effectively for water analysis and to take advantage of its simultaneous multi-element capability, continuous preconcentration of as many as possible target trace metals is required. The target metals are a group of potentially toxic metals found in raw and treated waters such as aluminum, chromium, cobalt, copper, iron, lead, manganese, mercury, molybdenum, nickel, strontium, vanadium, and zinc. The water samples also contain other metals at much higher concentrations such as sodium, potassium, calcium, and magnesium. In terms of toxic risk, these can be called irrelevant. Their presence, however, can cause serious matrix interferences in ICPES analysis.

Successful trace analysis of heavy metal ions requires the elimination of irrelevant but interfering hard metal ions. In this preconcentration procedure, the separation of the target metals from the irrelevant metals is being achieved through selective adsorption on a modified resin contained in a column. The resin is modified by the addition of a chelating ligand. The column can simultaneously provide an adsorbing medium for the target trace metals and an eluting medium for the irrelevant metal ions. Traditional methods involve collection of all metals, followed by the selective elution, coprecipitation or extraction of the metals of interest.

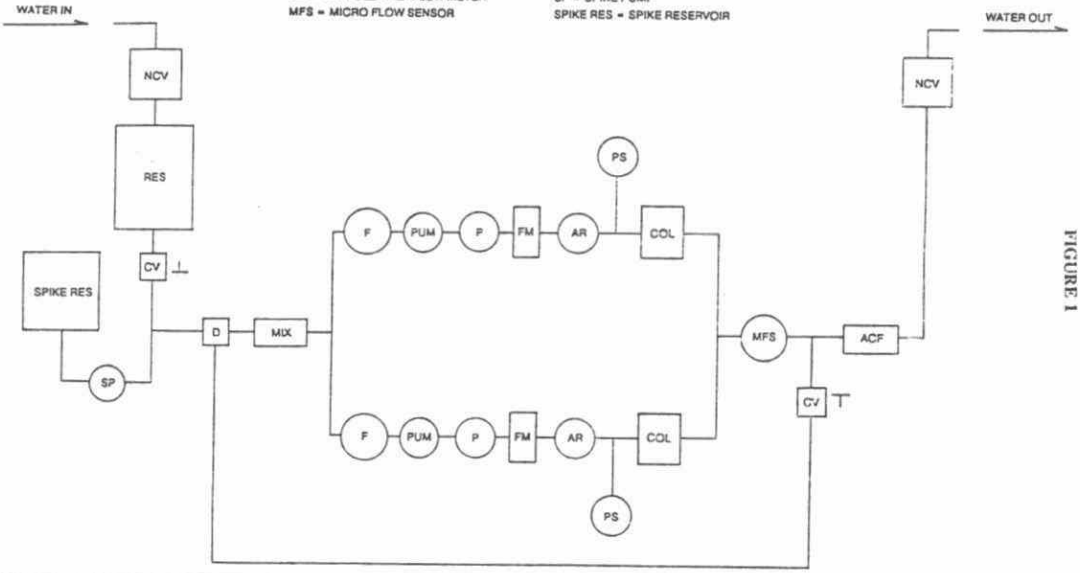
The differentiation of the irrelevant hard and the trace soft metal ions is possible because of their different complexing characteristics. The hard alkali and alkaline earth metals exhibit a preference for a hard donor atom, such as oxygen, for complexation. The soft heavy metals exhibit a preference for a soft donor atom, such as sulphur or nitrogen. Therefore, preferential complexation can be employed to separate hard from soft metals. To ensure that the undesirable metals are continuously eluted during the concentration of the heavy metals, the ligand should have soft nitrogen and sulphur donor atoms preferably used in combination with each other in a polydentate ligand.

The ligand-to-resin bond can be formed by varying the resin type and manipulating the terminal functional group on the ligand, to achieve various binding mechanisms. An adsorbent link is most applicable for the methodology desired in these studies, which requires fast batchwise resin preparation, flexibility in binding and elution of metals, and choice of elution products. In the desired binding mechanism the bidentate or chelate ligand is hydrophobically adsorbed to the resin to form metal complexes by covalent donor bonds. The adsorption of the ligand to the resin is strengthened by an electrostatic attraction between the hydrophobic aromatic structure of the resin and the hydrophobic aromatic portion of the ligand.

Some commercially available ligands that are possible candidates for the desired extraction are 2-mercaptopyridine, 2-quinolinethiol, 2-mercaptothiazoline and 2-mercaptobenzothiazole. Most recent literature has shown the ability of 8-mercaptoquinoline to preconcentrate micro amounts of elements in natural water. These elements include a wide range of metals from both group #2 and #3[1].

ACF = ACTIVATED CHARCOAL FILTER
AR = AIR BUBBLE REMOVER
CV = CHECK VALVE (1PSI)
COL = COLUMN
D = 3 WAY DIVERTER
F = FILTERS
FM = VARIABLE AREA FLOW METER
MFS = MICRO FLOW SENSOR

MIX = MIXING TUBE
NCV = NORM CLOSED VALVE
P = PRESSURE GAUGE
PS = PRESSURE SWITCH
PUM = MICRO PUMP
RES = RESERVOIR RAW WATER
SP = SPIKE PUMP
SPIKE RES = SPIKE RESERVOIR



FLOW CHART
APS-MKII O/M

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FIGURE 1

The type of resin chosen to be tested was XAD-4. This resin has been successfully used to support hydrophobic chelate ligands which coordinate using either 2 sulphur atoms or 1 sulphur and 1 nitrogen atom[2].

Experimental

The overall design of the trace metals preconcentration instrument is the same as that of the organic sampler. The major emphasis in adapting the design to one suitable for metal analysis is on the replacement of stainless steel components with Teflon or other organic materials such as polypropylene.

Initial tests were performed to determine which ligand yielded the optimum ratio of ligand to resin. Other considerations for the choice of ligand were the ease of resin preparation and shelf life of the loaded resin. Experimentation was performed using glass columns packed with 5 ml of the ligand loaded resin. All materials were soaked in concentrated nitric acid and thoroughly rinsed with deionized/distilled water. A 50 ml cocktail of five heavy metals - cadmium, chromium, zinc, copper and lead (1ug each) - and one of four undesirable metals - potassium, sodium, magnesium or calcium (10 to 300 ppm each) - in deionized/distilled water was applied to the columns. The columns were then washed with 50 ml of deionized/distilled water to simulate actual sampling conditions and to determine the retention of the hard and/or soft metals on the column. The columns were then eluted with 25 ml of 1% nitric acid and the samples were stored in polyethylene bottles. Solutions of methionine or cysteine in 5% nitric acid were also tested as possible eluting agents.

To determine the initial adsorption to the resin, when the metal cocktail was added to test column, the eluent from the column was collected and analyzed. Also collected were the subsequent water washings of the column.

Smaller aliquots of nitric acid (5ml of 1% nitric acid) were collected after being eluted from the column. This would indicate when the metals are eluted so that the amount of nitric acid required could be determined.

The capacity of the ligand loaded resin column for the five selected metals was determined by applying an equivalent of 2800ppb to the column(with 5mL of resin) in aliquots of 400ppb, 400ppb, 1000ppb and 1000ppb. The aliquot was collected after passing through the column. The subsequent water wash was also collected.

The capacity and elution of mercury was tested by applying a 100ppb mercury solution to the column and then eluting with 10, 20 and 50% nitric acid. The capacity of all the selected metals including mercury were tested with all metals in one solution.

Because of problems encountered with the flow sensor within the water sampler, namely that the flow rate represents the low end of the range of the flow sensor, tests were conducted to verify the possibility of increasing the internal flow rate of the sampler. For these experiments a column, manufactured for the sampler, was used in place of the glass testing columns. Using the ratio of bed volume to flow (bed volumes per minute), flows equivalent to 100ml/min and 200ml/min were achieved.

Studies with a new ligand, 2-aminobenzothiazole, were conducted. Metal adsorption and elution were determined.

Results

The ligand chosen was 2-mercaptobenzothiazole (MTB) since a ratio of 0.5 mmol ligand:1 ml resin provided the maximum concentration of ligand complexed on the resin. This ratio presents 2.5 mmol of ligand for every 5 ml of resin. The total amount of ligand attached to the resin is approximately 20% of the original quantity. The initial experiments of the column containing 100 grams of treated resin were performed with a 1 mL test sample containing 1000 ppb of cadmium. After a 50 mL wash and a 1 % nitric acid elution, essentially 90 % recovery was obtained.

Recoveries in the presence of sodium and potassium interferences were not affected significantly compared to interferences by calcium and magnesium. The recoveries of test ions following elution are variable with and without the presence of interfering ions. The extracts were analyzed for the presence of these interfering ions and none were found, indicating that these ions were not bound to the ligand at the time of elution.

Copper, zinc and chromium divalent ions yield low recoveries while those of cadmium and lead tend to be highest, particularly in the absence of interfering ions. Results indicate that of the three metals, copper, zinc and chromium, only copper is bound to the ligand in sufficient quantities, approximately 100%. Approximately 93 and 97% of cadmium and lead, repectively, were bound. This situation is unchanged in the presence of the alkali and alkaline-earth metals because these ions have very weak bonding to the chelating ligand.

Because of the high affinity of copper for the ligand, only approximately 9% is recovered. Cadmium and lead experience 100% recoveries.

For the elution step, 25ml of nitric acid are used. Tests revealed that most of the metal has been eluted within the first 15ml of the nitric acid. After 15ml of nitric acid, 98% of cadmium and 99% of lead were eluted.

The capacity of 5ml of ligand loaded resin was determined to be; Cr(566.0ppb), Cu(1358.9ppb), Zn(39.0ppb), Cd(168.1ppb), Pb(535.1ppb). The maximum possible capacity was 2800ppb. The resin did not show signs of exhausting its capacity for copper and so the actual capacity could be much higher. Mercury, like copper, was completely adsorbed to the column. The capacity of mercury was only tested with 100ppb, however the actual capacity is possibly much higher than this value. There was no elution of the metal with 10, 20 and 50% nitric acid.

When tested at the actual flow rate of the sampler, 100ml/min, the column exhibited adsorption values similar to those described above. However when the flow rate was doubled to 200ml/min the adsorption values dropped by approximately 20% for each metal. As was expected, the elution values are dramatically reduced when the flow rate was increased to 100ml/min and 200ml/min.

Tests with 2-aminobenzothiazole proved that the ligand did not have sufficient adsorption or elution abilities. No further tests with this ligand were conducted.

Discussion

The adaptation of the dioxin preconcentration sampler to the detection of trace levels of heavy metal ions has involved several major considerations. The first is the conversion of all internal surfaces from stainless steel to inert plastics to minimize the adsorption of metal ions or hydrated metal oxides to any hydrophillic surfaces. Another, is the adaptation of the filtering step to insoluble metal detection. Finally, of much importance, is the development of a suitable ligand for soluble metal ion detection.

The first step is completed and the fully adapted preconcentration instrument will be functional in the near future. The second step requires only the identification of filter materials similar to those used in the organic sampler which will not interfere with mildly acidic extraction processes required for metals. The adaptation of the column adsorbent procedures is the most important feature of this research. A technique is being developed to be transparent to irrelevant ions and thus, selectively capturing the heavy metal ions of interest. The adsorbent is treated with ion selective ligands in an effort to preferentially adsorb the trace ions at the 40 ppb level in a background of 10 to 300 ppm of alkali and alkaline earth metal ions.

The results show that MTB is an effective chelating agent in varying degrees for all of the test metal ions. It does not appear to bind either the monovalent alkali metal ions or the divalent alkaline earth ions but does appear to bind the target metal ions. The ligand also displays a large capacity for the metal cations tested, namely cadmium, lead and copper. The ligand is also capable of supporting metal chelation at elevated flow rates to 200ml/min.

The 1% nitric acid medium is adequate for effective elution of certain test ions, namely cadmium and lead. The work on this first ligand has provided evidence that the concept of selective trace metal ion capture is viable, and further work to optimize the ligand structure should permit the effective analysis of most toxic metals at or below the ppb level.

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DP8

Brominated and Mixed Bromo/Chloro Dibenzo-p-Dioxins and Dibenzofurans: Analytical Methods and Toxicities; D.S. Waddell, B.G. Chittim and J.M. Sparling, Wellington Environmental, Guelph, Ontario

Paper withdrawn

DP9

CHLORINATED AND NON-CHLORINATED ORGANICS STORAGE STUDIES

W.M. Neaves* and B.B. Fong
ENVIROCLEAN, 921 Leathorne St., London, ON, N5Z 3M7

The widespread implementation of programs to monitor and control trace organic contaminants has brought with it a need to refine sampling, storage and analysis protocols. Of key concern is the stability of the compounds of interest in various sample types during transport and storage prior to analysis. This information would be of value, both in developing valid sampling and analysis procedures and in planning monitoring programs. The objective of this study was to compile information from existing sources regarding the stability of a variety of sample matrix-organic compound class combinations to recommend optimum sample storage conditions where possible, and to evaluate the completeness of the information available.

Sample matrices studied were air-cartridge (AIR-C), air-SUMMA canister (AIR-S), air-filters (AIR-F), biota (BIO), drinking/surface water (DW), sediment (SED), vegetation (VEG), and waste waters (WW). Organic compound classes studied were acid extractable-phenolic (AE), base neutral extractable compounds (BN), carbamate pesticides (CP), chlorinated dibenzo-p-dioxins and dibenzofurans (DX), neutral chlorinated extractable (OC), organophosphorus pesticides (OP), acid extractable-phenoxy acid herbicides (PA), phenyl urea pesticides (PP), resin and fatty acids (RA), triazine herbicides (TR), volatile organics-halogenated (VH), volatile organics-non halogenated (VN), and volatile organics-sulphur compounds (VS). A listing of the number of data points obtained in this study for each matrix-class combination of interest is shown in Table 1.

Data was obtained from published stability studies. In some cases, information was extracted from other works which included sample stability aspects as a minor part. Unpublished sources of data were identified but very little of this information could be obtained.

Data obtained in the course of this study were compiled into a relational database. Storage recommendations were made after statistical analysis of this data. From Table 1, it can be seen that for some matrix-class combinations, the recommendations were made on limited data. For these combinations and for combinations where no data were obtained, recommendations for further experimental work were made. Methodologies for performing sample stability studies were examined with a view toward a standardized statistically validated approach in future work.

Table 1. Number of Data Points for Sample Matrix-Organic Compound Class Combinations

Compound Class	Matrix							
	AIR-C	AIR-F	AIR-S	BIO	DW	SED	VEG	WW
AE	0	0	0	* 24 *	937	0	0	0
BN	0	32	0	2	442	36	0	72
CP	XXXXXX	XXXXXX	XXXXXX	XXXXXX	8	10	38	0
DX	0	0	0	0	31	0	0	0
OC	4	0	0	264	844	14	14	11
OP	XXXXXX	XXXXXX	XXXXXX	* 7 *	48	2	55	5
PA	XXXXXX	XXXXXX	XXXXXX	XXXXXX	9	2	2	0
PP	XXXXXX	XXXXXX	XXXXXX	XXXXXX	0	XXXXXX	XXXXXX	1
RA	XXXXXX	XXXXXX	XXXXXX	XXXXXX	0	XXXXXX	XXXXXX	68
TR	XXXXXX	XXXXXX	XXXXXX	XXXXXX	4	9	6	0
VH	68	0	0	XXXXXX	158	18	XXXXXX	2
VN	50	2	0	XXXXXX	23	10	XXXXXX	0
VS	0	0	0	XXXXXX	XXXXXX	XXXXXX	XXXXXX	XXXXXX

* * - denotes combinations for which data was obtained and reported but not required.

XXX - denotes combinations not required for this work.

VOLUME II

SESSION E

ENVIRONMENTAL SOCIO-ECONOMICS

VERBAL PRESENTATIONS

E2

INFLUENCE OF VALUATION DISPARITIES ON JUDICIAL CHOICE AND LEGAL SANCTIONS

Jack L. Knetsch
Simon Fraser University
Burnaby, British Columbia V5A 1S6

Legal restraints and controls not only influence the actions of individuals, but continue to play a large role in the design of environmental policies. Consequently, the response to legal sanctions and rewards is an on-going concern to both judicial and regulatory approaches to environmental control -- in choices between injunctive and damages remedies, and in the design of policies and enforcement strategies.

The purpose here is to indicate the extent to which judicial choices and legal sanctions may be influenced by a heavier weighing of losses over foregone gains, and the acceptability or unfairness of actions that are rooted in such valuation disparities.

Conventional legal, as well as economic, analyses assume that people's willingness to pay to acquire or maintain entitlements and the compensation they demand to give them up, will yield equivalent measures of changes in people's economic well-being. However, empirical evidence from numerous controlled tests is not at all consistent with this traditional equivalence assumption (Knetsch and Sinden, 1984; Knetsch, 1989; and Knetsch, Thaler and Kahneman, 1989). The observations of large and persistent differences between economic values measured on

the basis of willingness-to-pay and compensation-demanded assessments of economic sacrifice, or value, together with the implications of such disparities, is now the subject of increased research attention (Knetsch, 1988; Smith, 1989).

The differing weights attached to gains and losses has also been found to influence people's judgments of what they regard as acceptable or unfair behaviour in economic relationships (Kahneman, Knetsch and Thaler, 1986). If an action is seen to impose a loss on one party for the benefit of another, this will nearly always be widely seen to be unfair quite apart from whatever economic justification might exist. For example, raising prices in response to sudden shifts in demand or cutting wages when unemployment increases, is judged to be unfair by vast majorities of people. A major motivation for these judgments appears to be that losses matter much more than foregone gains.

This strong intuition to value losses more than commensurate gains, and the implications for the resolution of competing legal claims, was summarized by Oliver Wendell Holmes in the following terms:

> "It is in the nature of man's mind. A thing which you have enjoyed and used as your own for a long time, whether property or an opinion, takes root in your being and cannot be torn away without your resenting the act and trying to defend yourself, however you came by it. The law can ask no better justification than the deepest instincts of man." (1897, p. 477).

Value Differences and Judicial Choices

Contrary to judicial choices that would result from an equal weighing of gains and losses, legal decisions over a wide range of conflicts reflect a systematic treatment of losses being much more important than foregone gains (Cohen and Knetsch, 1989). In these cases economic gains and losses are treated differently even though nominally commensurate.

In actions seeking recovery of lost profits, for example, legal rules make a consistent distinction between "loss by way of expenditure and failure to make gain". While permitting recovery of economic losses, judges are very reluctant to compensate for "lost profits" whether the claim is in contract or tort -- recovery of expenditures is permitted, recovery of foregone gains is not.

Another example where the valuation disparity manifests itself is in the distinctive treatment of performed and unperformed "intra-contractual promises". For instance, when a person promises to pay an additional sum for a previously arranged contractual performance, the courts have uniformly denied the promisee the right to enforce the promise. However, if the plaintiff not only agrees to pay but actually transfers the money, courts will generally not order the money returned unless extortion under economic duress can be demonstrated.

The circumstances are indistinguishable except for the location of the money -- whether the defendant is being asked to give back the money or forego receiving it.

Similar distinctions are found in many other areas of law. These seem part of a consistent pattern of judicial choices that result from weighing actual out-of-pocket costs far more than the opportunity cost of giving up a gain. While numerous law reform proposals call for rulings which would "reconcile" and eliminate such "illogical distinctions drawn by existing law", court decisions over a broad array of cases continue to reflect community standards of fairness and values and accord greater protection of losses.

The Coase Theorem and legal Sanctions

Many legal reform proposals, based on conventional assumptions of gain/loss value equivalence, call for more specific alienation of entitlements to promote more efficient resolutions of externality conflicts, and for greater use of injunctive remedies to allow parties to resolve conflicts by private negotiations. For example, in a case such as a kennel creating a nuisance in a residential neighbourhood it is often suggested that courts simply identify the property right as either an entitlement to allow disturbances or to preserve tranquility, and then encourage the parties to bargain to an efficient solution -- homeowners can pay the kennel operator for quiet if

they feel it worthwhile, or the kennel operator can buy off neighbours if such voluntary transactions will leave a suitable profit. Similar suggestions have been made to make land use zoning alienable and explicitly fungible, to promote private bargaining and efficiency.

These proposals are generally based on the conclusions of the Coase Theorem that, in the absence of transactions costs and wealth effects, people will voluntarily make any exchanges necessary to assure that resources are shifted to their most valued uses and that final arrangements of entitlements will not depend on original allocations or assignments. This prediction provides a strong motivation to worry less about which party is should prevail over the other, to make greater use of exchangeable entitlements and to avoid less flexible regulatory controls.

However, the predictions that all beneficial exchanges will be made, and particularly that final entitlements will be independent of initial assignments may be largely incorrect. The expected outcome of final allocations of rights not depending on initial legal positions, is based on the assumption of people attach equivalent values to gains and losses and belief that fairness notions have no influence on transactions. These are sharply at variance with empirical findings. The evidence of greater valuations of losses means that potential buyers will consistently value entitlements less than potential sel-

lers and this will greatly reduce the number of possible advantageous exchanges (Thaler, Kahneman, and Knetsch, 1989).

Implications for Legal Sanctions

Valuation disparities, of losses being more important than gains, appears to exert a major influence over legal decisions and the reactions to legal restraints. These differences, and their influence on perceptions of unfairness, are often not taken into account in proposed legal reforms or in the design of legal restraints on activities generating negative externalities such as environmental degradation. In contrast to traditional views of economic behaviour, the value disparities are very likely to have a large influence on people's reactions to the behaviour of others and to public policies and actions.

A more appropriate accounting of gains and losses would no doubt lead to changes in the design of legal controls and likely to their greater acceptance and effectiveness. For example, to the extent that changes can be effectively framed as foregone gains rather than losses, they are likely to be more acceptable. Similarly, redistribution of resources or entitlements may be less disruptive if it is not taken from one party to the direct benefit of another; but are instead designed to reimburse explicit costs borne by others or to be less than permanent in nature. And remedies for environmental losses may be of greater value if they mitigate or reduce the actual

losses or provide close substitutes rather than compensate in money or unrelated offsets (Knetsch, 1990).

On present evidence, some policy choices appear unnecessarily costly and generate acrimony that might be avoided with a better appreciation of the different impacts of gains and losses and the role of fairness judgments.

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E3

BENEFITS TO BEACH USERS FROM WATER QUALITY IMPROVEMENTS

By:

M. Fortin

Ecologistics Limited
Waterloo, Ontario

November, 1989

1.0 INTRODUCTION

Beach users will remember the summer of 1983 as an unseasonably hot and dry summer when an unusually high number of their favourite beaches were posted due to bacterial contamination. The resulting public and media outcry was answered in the form of the Beach Management Program of the Ontario Ministry of the Environment. Under this program, research into causes of the bacterial contamination identified sources such as combined sewer overflows, illegal sanitary connections to storm-sewers and the mismanagement of livestock manure. The solutions to these problems often came with a high price tag and little indication of the exact nature and magnitude of resulting benefits. Sound decisions could not be reached nor could priorities be established in the absence of a basic knowledge of how the demand for beach recreation would respond to water quality.

A ground breaking study was completed in 1987 that provided the basic structure of a planning tool to evaluate and prioritize site-specific remedial measures for Ontario beaches (Usher, Ellis and Michalski, 1987). However, in the absence of sound empirical research, the authors of this model resorted to ad hoc relationships to describe the response of beach users to changes in water quality. Moreover, they were not able to derive monetary estimates of the benefits associated with water quality improvements.

This paper describes a subsequent study, sponsored by the Ministry of the Environment, that undertook to fill some of the gaps in our understanding of beach user behaviour. Objectives of the study were:

- to monitor beach use and beach attributes, including water quality, over a recreation season at several Ontario beaches;
- to interview beach users concerning beach use behaviour and water quality perceptions;
- to develop and compare alternative measures of the value of water quality to beach users.

2.0 METHODOLOGY

Personal interviews were conducted with beach users at five beaches on Southern Ontario. None of these were major provincial beaches, rather there were two Great Lake and three inland lake beaches of local and regional significance. In total, 442 home-based, day-user parties were interviewed on 34 days over the period July 1 to August 16 in 1988. Respondents were queried about their use of the survey beach and other Ontario beaches, their perceptions of water quality conditions and other beach/park attributes, beach visitation costs and their socio-economic and demographic circumstances. The questionnaire also included open ended comment questions and questions related to contingent values and contingent beach use. The later questions invite the respondent to indicate how they would respond to or value a hypothetical change in water quality conditions.

At the time of the interviews, field staff also measured and recorded certain water quality and other environmental parameters that related directly to respondent perceptions such as water temperature, water clarity, incidence of posting, odour, presence of debris, and so on.

Descriptive statistics were prepared from the primary data and additional tests, relying primarily on regression analysis, were completed to examine the consistency of water quality perceptions, to identify factors that influence measures of respondent willingness to pay for water quality enhancements, and to develop travel cost measures of the value of water quality.

3.0 OVERVIEW OF BEACH USE

Thirty to 60 percent of all respondents at each of the survey beachs originated from a single large community near the beach. Their average one way travel time was 23 minutes and the average travel distance, 22 kilometres. Average party size was 4.1 persons of which 2.6 were family members. Across beaches, average party size ranged up to 5.9 persons at a beach featuring more family oriented activity. Fifty-three percent of all groups included children under the age of 12.

The mean length of stay at the beach was four hours with 91 percent of all visits lasting less than six hours. Travel time to the beach tended to increase with the length of stay at the beach (2-3 minutes for every additional hour spent at the beach). Presumably the longer stay made a longer journey worthwhile.

Among the activities that were pursued, relaxing and sunbathing were actually more popular (a 96 percent participation rate) than swimming (79 percent). Picnicking (60 percent) and people watching (61 percent) came next in order of popularity. Certain beaches featured specialized activities like hiking, cycling or wind surfing.

Average total out-of-pocket trips costs for the entire party were $22 comprising $4.80 for season passes, $7.60 for gas, entry fees and other unavoidable costs and $9.40 for rentals, meals and other discretionary costs.

4.0 WATER QUALITY PERCEPTIONS

Four of the five beaches received an average overall water quality rating lying between "fair" and "good", with the fifth beach being rated "very poor" to "poor". This last beach also received low respondent ratings for posting frequency, temperature and water clarity. The major category of comments on water quality expressed concern over generally poor quality conditions (31 percent of all comments). Other dominant comment categories dealt with algae (18 percent), water clarity (17 percent) and bacterial contamination (16 percent). No comments specifically addressed the issue of toxic substances.

Ratings of individual water quality indicators by respondents displayed a surprising degree of consistency with corresponding measurements of parameters related to those indicators. Perhaps not surprisingly, the strongest relationship was for postings (t-scores in brackets):

$$\ln(\text{POSTED RATING}/5) = \underset{(-0.937)}{-0.024} + \underset{(12.825)}{0.287} \ln(1 - \text{POSTING FREQ.})$$

Adjusted R^2 = 0.832, F-score = 164.5, no. obs. = 34

where: POSTED RATING = rating of posting frequency (0 = "all the time" to 5 = "never")

POSTING FREQ = proportion of days posted over the season (from 0.0 to 1.0)

A strong relationship is to be expected here considering the direct evidence of bacterial contamination provided beach users by placarding of beaches.

Correlation coefficients for other regression relationships in this series investigating individual water quality indicators are:

Temperature Rating	0.615
Rating of Wave Roughness	0.400
Rating of Water Clarity	0.263
Rating of Odour	0.336
Rating of Algae Density	0.407

In each case, explanatory variables were measures or interviewer ratings of features in the environment that could be perceived by beach users.

An strong result was also obtained when overall water quality ratings were regressed against respondent ratings of individual water quality indicators (t-scores in brackets, two stage least squares regression):

$$\ln(\text{OVERALL QUALITY}) = \underset{(0.48)}{0.17} + \underset{(1.55)}{0.31} \ln(\text{TEMPERATURE}) + \underset{(0.32)}{0.05} \ln(\text{WAVES})$$

$$+ \underset{(0.65)}{0.27} \ln(\text{CLARITY}) + \underset{(0.53)}{0.33} \ln(\text{ODOUR}) + \underset{(1.44)}{0.51} \ln(\text{ALGAE})$$

$$- \underset{(3.26)}{0.66} \ln(\text{POSTING})$$

Adjusted R^2 = 0.779, F-score = 20.34, no. obs. = 34
(two stage least squares regression)

All of the variables in this equation were scaled to lie in a (0,1) interval and in every case larger values represented higher quality ratings. Regression coefficients all fall within a (0,1) interval as expected. The

magnitude of each estimated regression coefficient is directly proportional to the significance of each explanatory variable in determining the overall magnitude of the quality rating. This suggests that beach closures have a predominant impact on respondent perceptions of beach water quality.

5.0 WILLINGNESS TO PAY FOR WATER QUALITY

Respondents were asked the question, "What is the most that you would be willing to pay, say as taxes, over the period of a year, to assure very good water quality at any Ontario beach you might want to use?". Out of 318 respondents who answered the question, 92 (28 percent) indicated an unwillingness or reluctance to pay anything and 13 (4 percent) were willing to pay but couldn't state how much. The majority of stated payment amounts fell below $100 per year and the mean and median payments were respectively $62 and $30 per year (estimates include amounts of $0.0 for those unwilling to pay, but exclude those who didn't know how much to pay). Six respondents stated amounts in excess of $500. The average payment amount was highest at that beach with the lowest water quality rating.

Respondent comments related to this question revealed a telling difference between those willing to pay something and those who weren't. Comments for the first group emphasized an environmental concern or an interest in supporting a good clean-up program (accounting for 53 percent of all comments from this group) while comments from the unwilling group emphasized an objection to more taxes or to government spending priorities (48 percent).

Regression analysis to explain willingness to pay amounts suggested the following:

- a stated concern with the payment mechanism was associated with a $30 reduction in payment amount,
- the payment amount increases by $8 for every $1000 in gross household income,
- the payment amount falls by $26 if there are children in the family (perhaps because there is less effective available income),
- willingness to pay increases with the total level of beach activity as measured by the total number of beach trips made by the respondent in 1987.

6.0 TRAVEL COST MODEL OF BEACH USE

Survey data were used to develop a generalized travel cost model of beach use. Mendelsohn and Markstrom (1989) describe this as a single equation model incorporating data from multiple sites. In theory, travel distances to alternative sites in such a model are assumed to be the same for all users. In practice, this condition is invariably violated and the model consequently ignores substitution effects at the risk of being subject to biased coefficient estimates. Time constraints precluded the option of developing respondent information for substitute beaches (though such a step could readily be taken given the available survey data).

Individual respondent observations were used in the travel cost regression analysis in this study rather than averages of respondent data for each origin zone as is customarily done. This preserved the full range of information that is provided by the individual respondent data. It did, however, introduce two sources of bias corresponding to the uneven clustering of respondents in larger origin zones and a uniform distribution of observations across beaches that experience quite different levels of popularity and that accordingly merit differing levels of representation in the statistical analysis. To overcome these sources of bias, a weighted least squares regression procedure was applied using the following weighting term:

(average no. of persons on beach "i")/(no. of households in origin"j")

The dependent variable was defined as reported trip frequency to the survey beach in the year prior to the survey (1987). A variety of exploratory regressions were completed to identify appropriate functional form, significant explanatory variables and interactive effects between these variables. Goodness of fit statistics and t-scores on individual coefficient estimates provided the basis for decisions at this stage.

This exploratory regression analysis led to the following conclusions:

- the best set of explanatory variables included unavoidable out-of-pocket trip costs, the opportunity costs of travel time for employed household members, overall water quality ratings (QUAL, 1 to 5 rating variable ranging from 1 to 5), a beach crowding variable (CROWD, average mid-day count of persons per meter of beach length) and gross household income (INCOME, $000's/year)
- the opportunity cost of time should be discounted by a factor of 0.12 in defining total trip costs, i.e.: COST = (out-of-pocket costs) + 0.12 (opportunity costs)
  (COST is measured as the per trip cost for the entire household)
- the COST and QUAL variables demonstrate a significant interaction.

The final regression equation that was adopted for subsequent analysis was (t-scores in brackets):

$$\begin{aligned} \text{TRIPS/YR} = {} & -1.515 - \underset{(-10.288)}{0.273}\,(\text{COST} * \text{QUAL}) + \underset{(9.648)}{3.921}\,\text{QUAL} \\ & \underset{(-3.290)}{-1.623}\,\text{CROWD} + \underset{(2.113)}{0.059}\,\text{INCOME} \end{aligned}$$

Adjusted R^2 = 0.281, F-score = 37.841, no. obs. = 378

6.1 Consumer Surplus Calculations

The households consumer surplus measure of value for annual beach visitation activity is measured as the area under the demand curve and above the price line. This calculation was completed for each respondent separately using individual respondent measures for each independent regression variable. This approach was used in order to have respondent consumer surplus value information that was directly comparable to

the individual measures of willingness to pay. In undertaking the analysis, the estimated demand curve was first shifted horizontally by the amount of the regression error term for each respondent so that the curve would pass through the respondent's (COST, TRIP/YR) data point. This procedure implies that the error term for each respondent captures the influence of unexplained factors on demand. It also assumes that the influence of these factors is independent of price.

The consumer surplus calculation was also repeated for each observation using responses to contingent questions eliciting information regarding:

- how often respondents would travel to the survey beach under conditions of very good and very poor water quality,
- how far, at most, they would travel to reach the survey beach under existing quality conditions and if water quality were very good or very poor.

Responses to these questions provided a direct means of determining each respondents demand curve since they effectively identify the y-axis and price line intercepts for each demand curve. By assuming a linear demand curve, the contingent measures of consumer surplus can then be calculated in the same manner as for the linear travel cost curve.

Alternative estimates of consumer surplus are provided in Table 1. Both sets of estimates display a positive skew with the majority of values clustered below the means.

There is considerable disparity for low water quality, between the contingent beach use and travel cost model estimates of consumer surplus. Moreover, the travel costs model estimates display much greater variability than the contingent beach use estimates.

The value of a change from existing to very good water quality can be measured as the difference in the total consumer surplus for beach visits under existing and very good quality conditions. Based on the means in Table 1 these differences are:

Travel Cost Estimates	- $68
Contingent Beach Use Estimates	- $90

These values are in relatively close agreement with each other and with the willingness to pay value of $62 reported above. Note that they represent an annual household value associated with all of the household's beach visits; they are not a user-day value for water quality improvement.

TABLE 1

ALTERNATIVE ESTIMATES OF THE VALUE OF ANNUAL HOUSEHOLD BEACH VISITS FOR DIFFERENT LEVELS OF WATER QUALITY

BASIS OF ESTIMATE	Consumer's Surplus Estimated with[1] a Travel Cost Demand Curve			Consumer's Surplus Estimated with[1] Contingent Measures of Beach Use		
WATER QUALITY CONDITION	Very Poor	Existing	Very Good	Very Poor	Existing	Very Good
Average	$100	$111	$179	$4	$24	$114
St. Deviation	$340	$343	$493	$17	$61	$290
Minimum	$0	$0	$0	$0	$0	$0
Lower Quartile	$0	$0	$0	$0	$0	$10
Median	$0	$2	$11	$0	$3	$28
Upper Quartile	$25	$45	$100	$0	$15	$89
Maximum	$2931	$2931	$3997	$146	$586	$3 671
No. Obs.[2]	358	363	332	272	272	272

NOTES:

1. Monetary values ($1988) represent the value assigned by respondent households to their joint beach visits over the period of a year (one visit is a visit by all household members).

2. Numbers of observations vary as a result of omissions due to missing values for certain observations and also due to deletions of outliers and data from respondents who appeared not to understand survey questions.

7.0 DISCUSSION

The analysis reported above strives to throw some light on various empirical issues related to amenity valuation as well as filling key gaps in our understanding of beach use behaviour in Ontario. The results are at times promising, but there remain major shortcomings that likely frustrate the reader as much as they have the author.

Some success greeted efforts to understand water quality perceptions. Earlier research efforts have had only limited success in incorporating water quality into recreation studies (Freeman III, 1979; Turner, 1977). Many of the difficulties have been attributed to water quality data that was ill suited to the analysis. In this study, careful attention was given to collection of a complete set of both user perception data and related water quality indicator measurements. The analysis of resulting data led to a conclusion that water users can formulate reasonable impressions of water quality conditions that are consistent with reality. Moreover, the data analysis suggests that these impressions appear to influence recreation demand in a significant way. Providing users with information in the form of posting at beaches is a key element in fostering accurate perceptions of water qualtiy conditions.

In his popular book on environmental economics, Freeman (1979) identifies a need for empirical research on the relationship between travel time and the length of stay at a recreation site as well as on the marginal utility value of travel time for recreation. This study investigates of both of these issues. Travel time was found to be positively but weakly related to the length of stay. Regression results suggested that the value of recreation travel is only 12 percent of the wage rate, rather than 25 percent to 50 percent as found in commuter time travel work. These findings require and verification.

Three different approaches were used in estimating the value of improvements in water quality - a contingent value approach, a travel cost model and an approach based on contingent use data.

All three approaches are in surprising agreement about the value of a water quality improvement. This is of course comforting, but it doesn't necessarily mean that the findings are right. The travel cost estimates are likely biased due to a failure to consider substitutes within the model. The willingness to pay estimates show evidence of payment vehicle bias, and a quantification of this effect was possible. The estimate of benefit based on contingent use data show promise, but the general approach deserves some careful thought in order to evaluate its properties. Overall, however, the findings do provide a base of empirical information on beach use behaviour and beach user benefits. Moreover, the beach user survey database developed in this study offers further opportunity for research into the linkage between recreation behaviour and water quality.

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E4

VALUATION OF WATER QUALITY IMPROVEMENTS

Anthony Bruno and Patricia Blyth
Policy and Planning Branch
Ontario Ministry of the Environment

ABSTRACT

Quantifying and valuing the economic benefits that would result from improvements in water quality is a challenge for researchers and policy makers. The process involves unravelling complex linkages in an environment where information is often incomplete and relationships not fully understood. Studies which have attempted to evaluate changes in water quality have defined two types of economic benefits associated with an improvement in water quality: benefits which accrue to individuals who use the water and benefits which accrue to individuals who place a value on the knowledge that the water is cleaner. This paper focuses on the steps that are involved in trying to quantify and value these types of economic benefits. Examples of how studies have tackled this problem are also presented.

LINKAGES BETWEEN CLEANER WATER AND USE

Policy makers are faced with important decisions concerning desired levels of water quality and expenditures on control activities. In terms of policy development, it is important to know how expenditures to improve water quality will ultimately translate into benefits for individuals, communities or society as a whole. An attempt to value these benefits will assist decision-makers in identifying the series of trade-offs among water quality levels, expenditures required to obtain those levels, and the different uses that result.

Conceptually, the problem is relatively straightforward and simple. A particular water body is polluted thereby precluding certain end uses and the overall feeling that the water is not clean. The introduction of pollution control activities are required to improve the quality of the water allowing various water use activities to be restored. However, it will be shown that in reality the problem is far from simple.

The benefits of improving water quality differ from other environmental goods such as air quality in that improvements in water quality translate into a number of end uses

including: swimming, fishing, boating, commercial fishing and more passive recreational activities such as bird watching, and picnicking near the share. In addition, there are other intrinsic benefits unrelated to water use that also require quantification.

Intrinsic benefits arise from knowing that the improved water quality level will be preserved for our personal future use as well as for the use of future generations. Intrinsic benefits include option, existence, and bequest values. These intrinsic benefits are not restricted only to persons surrounding a particular water body, but could also be held by individuals on a provincial, national, or even global scale. These use and intrinsic concepts of value are further elaborated in Table 1.

TABLE 1

1. "Use Values" are held by individuals who have an increase in welfare by actually using the cleaner water, for example, swimming or sportfishing.

2. "Intrinsic" value which arises from knowing that the water is cleaner and the option of participating in enhanced recreational opportunities. Intrinsic value can be subdivided into:

   - Option value refers to an "insurance" value associated with maintaining the option to use the resource in the future.

   - Existence value refers to the value placed on knowing that conditions have been preserved or improved.

   - Bequest value refers to the value placed on being able to pass on to the future generations better environmental conditions.

Measuring the value of recreational use and intrinsic benefits to society is problematic because these goods or services cannot be purchased or sold in markets as are cars or clothing. Environmental goods are classified as non-market or "public" goods which unlike market goods, do not have a specific price attached to them. Therefore, non-market goods such as water quality cannot be divided into separate units and are available to many people at the same time. Market or "private" goods are separate units which are purchased by individual buyers. For example, if one person buys an apple and eats it, another customer cannot buy the same apple. The lack of a formal market makes it difficult to place a price on public goods.

Quantifying and valuing the economic benefits that stem from pollution control activities involves consideration of the following relationships:

- The effect of the implementation of control activities on pollutant loadings.
- The relationship between the reduction in discharge of particular pollutants and the change in water quality.
- Translation of the change or improvement of water quality into a change in use.
- The relationship of the increase in use in terms of physical units and the monetary value of these units.

The first two relationships are non-economic in nature and deal primarily with physical and biological processes. When pollutants are discharged into a watercourse, they enter a complex biological and chemical system which may result in the transportation, degradation and transformation of the contaminants. For example, when organic wastes enter a water course, they are degraded by bacteria. This reduces dissolved oxygen levels (a measurable component of water quality) to an extent and at a rate that depends on water temperature, wind, river flow rates and other physical and biological characteristics of the water body (Kneese, 1984). To further complicate matters, a reduction in one pollutant may affect one use favorably while affecting an alternate use in a negative manner. Because of these inter-relationships, it is difficult to establish a direct linkage between the contaminant discharged and its affect on water quality.

Water quality models have been used to predict how a reduction in a certain contaminant affects indicators of water quality, but often, such models are limited to the prediction of the effect of a change in only one aspect of the ambient conditions, such as dissolved oxygen (Kneese, 1984 and Marshall Macklin Monaghan, 1988). More complicated interactions often cannot be characterized. Moreover, these models cannot often definitively link the level of pollutant reduction to desired uses. It is an area of research that has just begun to touch the surface of the problem.

The third linkage brings together biology and economics. The biophysical indicators of water quality are translated into an increase in recreational or commercial use of the water body. As discussed above, the complexities of the physical, chemical and biological processes of the water courses often make it difficult to establish an explicit linkage between water quality and use. Making this linkage is essential in analyzing and valuing economic benefits.

The last linkage draws upon economic theory to aid in assigning a dollar value to an increase in use. These latter two relationships are the focus of this paper and are discussed separately below.

TRANSLATING IMPROVEMENTS IN WATER QUALITY TO AN INCREASE IN USE

To value the benefits associated with each level of water quality requires an estimate of the increase in use of different activities and the value of that increase.

Improvements in water quality may give rise to an increase in recreational activities in two ways: new activities may be made possible, while existing activities may be made more enjoyable. In the literature, most studies do not estimate benefits from enhancing the activity. Therefore, this discussion will be limited to the valuation of new activities.

A variety of methods have been employed in the literature, some using sophisticated techniques, with others relying heavily on professional judgement. One technique is to estimate the change in participation by means of regression analyses. This method was applied in a national study on fishing in the United States. A telephone survey of 300,000 individuals was conducted to determine whether individuals participated in fishing. The data were then used in regression analyses to project fishing as a function of water quality (Vaughan and Russell 1982). It was estimated that for the U.S. the total user-days per year of fishing would increase by 11,000,000 as a result of water improvements due to the introduction of the U.S. Federal Water Pollution Control Act.

Another method is to apply elasticities to the current number of user-days. A recreational use elasticity represents the responsiveness of activity levels to different quality levels. This provides an estimate of the change in user-days that would result from an improvement in water quality. A study on recreational benefits in Ontario used this method to estimate the increase in recreational days that would result from a 25% reduction in phosphorous. Using literature based elasticities, it was estimated that user-days for recreational activities would increase by a total of 50,000 for six lakes (DPA, 1987).

Sometimes, other rather inventive methods have to be found when limited information exists. One study based their estimates on the actual fish yield that would result if certain control technologies were implemented (Marshall Macklin Monaghan, 1988). It was estimated that implementation of these control measures would result in an

increase of between 2,700 and 5,600 angler-days per year. Another study based its estimates on the difference between current use and potential use in an environment which was unconstrained (APOGEE, 1989). The potential use figures were obtained from a provincial survey (Metropolitan Toronto, 1987). While their figure for user-days is an overestimate of the actual user-days that would result in a constrained environment, it does provide a gross estimate of the likely magnitudes.

It is recognized however, that there are other factors unrelated to water quality which will constrain demand and restrict participation at a local level. For instance, in Northern Ontario, the cold temperature of the lakes preclude swimming regardless of the quality of water. Access is often another problem unrelated to water quality. The availability of substitute activities located nearby may influence use of the water body. Lastly, perceptions play a key role in determining use. People may not swim because they believe that the water is unsuitable even though from a biological standpoint, the water is safe for swimming. A number of quality factors that appear to influence recreation are described in (DPA, 1987). These include catch rates and type of species for fishing and water clarity for swimming as some factors that influence these particular uses. Some studies have adjusted their results using professional judgement to include some of these factors, however, more research in this area would begin to bridge the information gap and would produce harder and more credible benefit estimates.

VALUATION OF BENEFITS

Economic theory provides us with the required tools and methods to estimate the monetary value of both user-days and intrinsic benefits that result from improvements in water quality.

Economics attempt to quantify changes in an individual's well being induced by changes in the consumption level of a good using monetary values. The monetary measure of consumer benefits or "welfare" of improvements in water quality is associated with an increase in the quantity of cleaner water. An investment in pollution control measures would lead to the public good of "cleaner water" which would result in the creation or enhancement of end-uses. In making decisions regarding the levels of investment required for control activities, the value of water quality improvements needs to be quantified.

Economists refer to "consumer's surplus" as an economic measure of value which shows changes in an individual's well being from changes in the level of water quality. Consumer's surplus can be described as the maximum amount of money an individual would be willing to pay for a certain good above

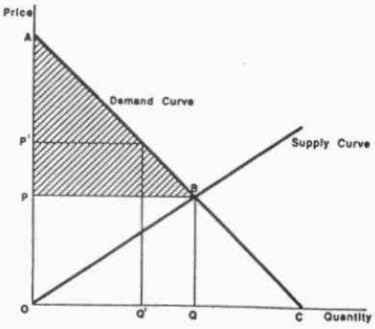
what the consumer is already paying for it. The individual would be willing to pay a higher price over and above the current price of the good in order to continue consuming it rather than giving it up. The maximum willingness-to-pay (WTP) represents this additional benefit or value the consumer gets. The actual amount the individual spends on the good would never be greater than the individual's WTP. Therefore, the surplus value, or the difference between the maximum WTP and actual expenditure, is referred to a consumer's surplus.

The concept of consumer's surplus for a traditional market-traded good is illustrated in Figure 1. Demand curves can be used to measure maximum WTP, actual expenditures, and consumer's surplus. The demand curve is made up of a series of price-quantity pairs of points for a particular commodity. The demand curve is downward sloping because it demonstrates the relationship that as the price an individual pays to consume an additional unit of a good increases the individual will consume less of the good.

In Figure 1, if an individual were charged price P for each unit of Q, expenditures would equal the area under the demand curve POQB. However collectively, individuals would be willing to pay a price higher than P. Thus, individuals total WTP is represented by the area AOQB. Consumer's surplus equals the difference between these two quantities under the demand curve APB. The value of area APB represents WTP or "economic value" of the good which is associated with the concept of valuing benefits.

Figure 1

THE CONCEPT OF ECONOMIC VALUE - CONSUMER SURPLUS

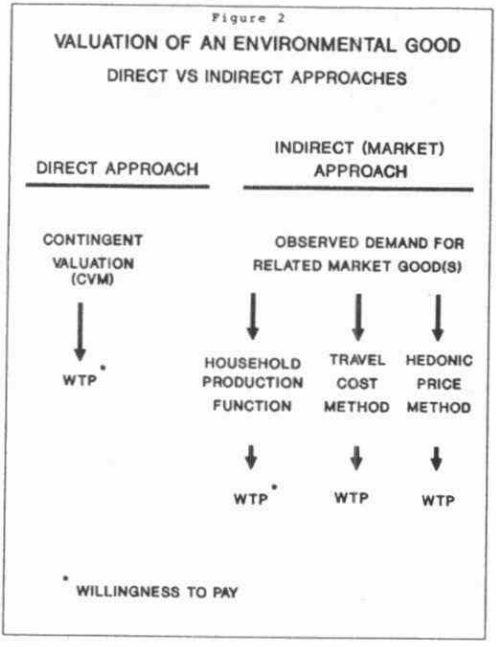


As mentioned earlier, since water quality is a public good, a unit price for the good cannot be easily determined. However, it is clear that people value clean water. Studies relating to water quality have used a variety of economic tools or methods to estimate consumer's surplus associated with improvements in water quality. The next section concentrates on some of these methods.

Economic Valuation Methods

The methods can be grouped into indirect and direct approaches which are illustrated in Figure 2. These methods which estimate the value of consumer's surplus incorporate a complex set of assumptions which are specific to the site studied and the population who can or will utilize the water body for various activities.

Figure 2



Indirect Valuation

Indirect methods attempt to infer implicit values for water quality changes based on the prices of private goods and services. One approach is the hedonic price method (HPM), which attaches monetary values to environmental goods through the analysis of housing markets. This method relies on actual observed real estate prices and behavior that individuals undertake in response to the effects of changes in water quality. In other words, changes in water quality levels would affect an individual's decision to buy or sell a home since the level of pollution in a water body will ultimately affect the price of the surrounding properties.

Another approach is the travel cost method (TCM), which estimates the demand for recreational activities. This method estimates WTP for recreational activities from the costs of travel and time incurred in getting to the site.

A third method is the household health production method where monetary estimates of health damages associated with water pollution are derived. A functional relationship is developed between human health attributes, exposure to water pollution, and expenditures on private goods (such as pollution abatement equipment and medical services) which minimize health risks.

Direct Valuation

A direct approach in valuing improvements in water quality attempts to elicit consumer's valuations through survey interview methods. The contingent valuation method (CVM) relies on the individual responses of a cross section of the affected population on their willingness to pay for a given improvement in water quality which increases and/or enhances various recreational uses. The approach may also be used to determine amounts individuals would be willing to pay for avoiding a deterioration in the level of water quality.

These direct and indirect methods have been employed in studies to estimate consumer's surplus. Table 2 shows the range of values for a fishing day that have been estimated by various studies. These estimates of consumer's surplus were derived using the direct survey approach or the travel cost method. The economic value of one day fishing ranges between $6 and $95. The lower dollar estimates may be more representative of the value associated with waterbodies that do not achieve an edible sportsfishery. The higher values may represent excellent fishing conditions where high populations of sport fish, such as trout and bass, are stocked. The range could also be attributable to the location and characteristics of the fishing experience, or the methodology employed in the study. Studies estimating

consumer's surplus usually incorporate a set of assumptions and descriptions which are largely specific to the sites being examined. For these reasons, it is preferable to conduct primary data and research on WTP.

Table 2

ESTIMATES OF CONSUMER SURPLUS ASSOCIATED WITH RECREATIONAL FISHING (USE VALUE) (in 1987 Canadian Dollars)

Activity Being Valued	Location	Consumer Surplus per Fishing Day	Source of Estimate
Recreational Fishing	6 Ontario lakes	$11	DPA Study
Salmon Fishing	Victoria, B.C. Campbell River, B.C. Sechelt, B.C. Port Alberni, B.C. Campbell River Guided	24 40 47 83 95	DPA Study
Recreational Fishing	Alberta	31	Adamowicz and Phillips
Recreational Fishing	Haliburton/Muskoka Region, Ontario	23	Victor and Burrell
Angling	Lake of the Woods, Ontario	6	Hough, Stansbury and Michalski
Trout Fishing Catfish Fishing	Fee-fishing sites, U.S.A Fee-fishing sites, U.S.A	33 21	Vaughan and Russell
Fishing	Adirondacks, N.Y	43	DPA Study
Fishing	Snake River, Idaho	25	DPA Study

Source: Marshal Macklin Monaghan Ltd, Assessment of Proposed Remedial Action Plans for Hamilton Harbour, 1988.

However, primary information and research is not always possible due to budget constraints or a short study time-frame. In these cases, studies have used values from the literature in benefits estimation. If this method is used, a careful examination of the assumptions and the site specific characteristics used in the study is necessary to ensure that the values applied will correspond to similar type experiences and conditions. For example, a study completed by Marshall Macklin Monaghan Limited (1988) applied a range of values from the literature to their estimates of increased user-days of fishing activity. A range of between $6 and $40 was selected to represent the economic value of one day of fishing. Higher estimates were eliminated because it was felt that they represented exceptional fishing conditions which would not be comparable

to the conditions at the Hamilton Harbour site. Based on their estimate of 5,650 angler days and providing that specific control measures were implemented the total annual use value from fishing was estimated as $130,000 per year.

It should be noted that when estimating the consumer's surplus for recreational fishing, two further complications are encountered:

1. Distinction between types of species.

2. Distinction between edible and non-edible fish.

Generally speaking, trout, bass, walleye, (sport fish) are more preferable than fishing for groundfeeders such as carp. These species would presumably be valued higher by anglers. Also, it is likely that being able to eat the fish would also result in a higher economic value. This could be a result of two factors: participation increases because the fish are edible and/or the economic value increases because they are edible. Unfortunately, no studies to date have distinguished between a sport fishery and an edible sport fishery. In the Marshall Macklin Monaghan study, the author recognized that higher values may be placed on edible fishery. No attempt was made to adjust any results because it was not clear to what degree the estimates of consumer's surplus would vary according to whether the fish was edible or non-edible.

Estimating intrinsic benefits is similar to estimating the value of user benefits except that defining the population area for the purpose of quantifying economic value is more problematic. This occurs because the population affected is not limited to only users of the water body.

Conceptually, it is feasible that a larger population would be willing to pay something to either preserve the lake, have the option to use it in the future or have knowledge that the water is cleaner. The question becomes what area is most realistic for estimating an increase in intrinsic value. There are a variety of possibilities that could be investigated. The Marshall Macklin Monaghan study (1988) applied estimates of value to the number of households in the Regional Municipality of Hamilton-Wentworth and the City of Burlington. The study did not attempt to estimate intrinsic values for a larger target area even though it is also feasible that every household in Ontario places some value on improving the water quality level at Hamilton Harbour. How would economic value differ among these two groups? It is possible that residents near the water body would value it more than residents living further away from the water body. Unfortunately, it would be difficult to estimate these differences without collecting primary data.

Table 3 illustrates the range of intrinsic values that have been estimated in the literature. Currently, only the contingent valuation method has been used to estimate intrinsic values. The number of studies estimating these types of benefits is far less than for use benefits, partly because it has only been recently that intrinsic benefits have been recognized as "real" benefits that require quantification.

TABLE 3

ESTIMATES OF INTRINSIC VALUES
(1987 Canadian Dollars per Household per Year)

Non-Use Values	Option	Existence	Bequest	Total
Greenley, Walsh & Young*	$ 37	$ 41-56	$ 28-53	$ 106-146
Smith and Desvousges:**				
From boatable to fishable	18-33	n/a	n/a	n/a
From boatable to swimable	34-44	n/a	n/a	n/a
Marshal Macklin Monaghan				
From Boatable to fishable	n/a	n/a	n/a	$ 87-146
From boatable to swimable	n/a	n/a	n/a	$ 103-153

* The lower estimate of existence and bequest values relates to non-user household only; the upper estimate are from user and non-user households combined.

** Estimates derived using iterative bidding from $125 are not included in this range since they are considerably higher than all other estimates.

Source: Marshall Macklin Monaghan Limited, Assessment of Proposed Remedial Actions Plans for Hamilton Harbour, 1988.

Several reasons for the range in values are discussed in (APOGEE 1989). Differences are cited in:

- methodology among the studies
- the size and characteristics of the water bodies of concern
- the magnitude of the proposed changes in water quality and the ways in which these quality changes are described
- alternatives available to the individuals being surveyed with respect to water based recreation, the distance that must be travelled to get to cleaner lakes to rivers which offer these opportunities
- whether a value is being placed on improving water conditions or preventing their deterioration

Estimates of intrinsic value are indicative of the magnitude of the likely benefits that would result from improvements in water quality. These estimates will become more credible as more research is conducted and the techniques and approaches employed tested and improved.

CONCLUSION

Estimating the benefits of expenditures on pollution control measures for given measures in water quality is not an easy task for today's policy-makers. This paper has shown that there are a number of problems and limitations on both sides of the equation - the biological/engineering sphere and the economic analyses. It is recognized by researchers that this problem is indeed complex. More work is required in all the disciplines but especially in providing information on translating the pollution reduction into improvements in water quality and into improvements in use. This would allow the production of more credible and useful benefit estimates.

Benefit estimation is a valuable component of the decision-making process and allows us to have a sense of what control measures are buying us in terms of improvements in environmental quality. This is a difficult concept for most to comprehend, but it is used almost everyday when decisions are being made. The only difference being, the benefits we are trying to value pertain to goods which are not traded on the market place. Does this mean that they have no value? Clearly people do place a value on cleaner water, cleaner air, trees, and parks. In order to allow policy makers to

make informed decisions regarding the allocation of resources, these values, whether user or intrinsic need to be incorporated into the decision-making process to portray a more balanced picture of the problem.

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E5

SOCIAL IMPACT ASSESSMENT IN WASTE MANAGEMENT PLANNING

WHERE ARE WE AND WHERE ARE WE GOING?

Ann M. Joyner, M.E.S., M.C.I.P.
Senior Environmental Planner
M.M. Dillon Limited
Consulting Engineers, Planners and Environmental Scientists
47 Sheppard Avenue East
Willowdale, Ontario
M2N 6H5

Waste management planning has reached a point where the focus is on waste reduction, re-use and recycling initiatives that minimize the requirements for unwanted landfill and combustion facilities. Despite this integrated approach, such facilities are usually a part of waste management plans. The consequence of this is that some communities must bear a larger burden of environmental impacts, human health risks and costs in order to benefit the entire community.

The social impact analysis that is part of the environmental assessment process should anticipate, analyze and assess the significance of these effects. Most importantly, the studies should ensure that recommendations to mitigate effects are incorporated into the design and include procedures to respond to the unequal burden placed on the host community.

It is now timely for the industry to step back and review what we have learned in the social impact assessment field for waste management. We can use this knowledge to plan ahead before facilities are targeted and anticipate the perceived and real effects that will face a host community.

In the following minutes I will review the key steps currently undertaken in social impact assessment for waste management projects with reference to specific studies completed by M.M. Dillon Limited. I will then summarize the benefits of SIA and some central issues arising from the social assessments. Finally, I will present some ideas regarding the future of social impact assessment in waste management planning.

The context for waste management planning in Ontario generally falls into two categories. Either the project is being undertaken as a waste management master plan under the Environmental Assessment Act (EAA) or it is undertaken under the Environmental Protection Act (usually requiring an EA Act exemption). Often projects are undertaken under both acts. In any case, it has been our experience that a broad definition of the environment encompassing social, natural and economic aspects of the environment (basically as defined in the EAA) is applied for all recent waste management projects. It is this context that I will refer to in my remaining time here.

WHAT IS SOCIAL IMPACT ASSESSMENT?

Social impact assessment is a description of social change that is the direct or indirect result of a proposed policy, program or project. The objective is to predict social impacts and suggests ways to control, manage or reduce effects while giving consideration to the views of the public. A key aspect of social impact analysis is not only to identify ways to mitigate effects but to deal with residual effects of waste management projects on the host communities.

KEY COMPONENTS OF SOCIAL IMPACT ASSESSMENT IN WASTE MANAGEMENT PLANNING

The following outlines the key components of social impact assessment (SIA) in waste management planning focusing on facility siting within an environmental assessment framework.

1. SIA in selection of candidate areas for facility siting (usually involving constraint mapping exercise).

2. SIA in selection of sites within candidate areas.

3. SIA in site comparison.

4. SIA in detailed site assessment for the preferred site.

5. SIA in recommendations for mitigation, monitoring and development of compensation policies.

TYPICAL SIA APPLICATIONS IN WASTE MANAGEMENT PLANNING

a) Site Selection for Landfill

Hawksbury and Northumberland Waste Management Master Plans and Domtar Wood Residue Disposal Environmental Assessment

Factors were selected to measure displacement of and disruption to residents and community features. Portions of the study area were excluded where major effects were expected. A progressively increasing level of detail was applied as smaller site areas were identified from within the larger candidate areas. For comparison of candidate sites the number of residents and community features within the site vicinity impact zones and along access routes was considered as well as characteristics/location of the residences and features.

For the Domtar wood residue study, consideration may also be given to distribution of benefits from the Cornwall paper mill (the source of the waste) to surrounding municipalities which are potential host communities.

The information for these factors was tabulated and/or mapped as appropriate for the specific site selection stage and the information was considered in establishing sites and comparing among sites. At the site comparative evaluation stage, mitigation measures and net (residual) effects were identified for each factor for each site.

In each waste management project the social assessment factors were considered highly important and influenced final siting decisions. In addition, proposed mitigation measures were carried forward to the final design stage.

b) Detailed Assessment

Private Sector (BFI) Medical Waste Treatment Facility (Under EAA) and Detailed Assessment of Preferred Sites for Landfill Projects (Under EAA and Environmental Protection Act)

A detailed social assessment was undertaken for development of a proposed private medical waste incinerator facility for a preferred site location. The data were obtained from secondary source information and face-to-face interviews with key community contacts. Factors applied in the assessment included displacement and disruption of residences and community/recreation features. Consideration was given to the definition of the local community, community character, response to the proposal, noise, visual, air quality and traffic effects. Specialist consultants were added to the team to assess each of these disciplines in detail. The results of the analysis were used to determine the overall acceptability of the proposal and to develop recommendations for mitigation measures.

The detailed social assessments undertaken for landfill sites under the EAA and Environmental Protection Act also use a multi-disciplinary team. Data are obtained through secondary sources, face-to-face interviews with surrounding residents (usually within 500 m of the proposed site), key informant interviews and workshops. Displacement and disruption to residents, community/ recreation features and the community are assessed. An economic analysis is undertaken in parallel covering local and municipal economic effects. The results of the analysis are used to determine the overall acceptability of the proposal and to develop recommendations for mitigation and compensation measures.

c) SIA in the Resolution of Conflicts in Waste Management Planning

Essex County Landfill No. 3, Landfill Expansion (Under the Environmental Protection Act)

In a recent short-term landfill expansion project in Essex County, the social analysis and public participation programs contributed significantly to the resolution of major areas of conflict prior to the EA Board Hearing. In this case, the ongoing Public Liaison Committee functioned to identify a final contour plan and waste reduction program that was considered to be

acceptable to the host municipality. The Liaison Committee and the results of a public workshop on visual effects helped to establish the basis for an agreement among the major waste producer, proponent and host municipality as to an acceptable continued use concept and a compensation package to offset residual effects.

The community impact assessment also identified numerous design and operations procedures that will be necessary to ensure that social impacts are kept to acceptable levels. For example, measures to control dust, odours, litter, noise and visual intrusion were identified. The SIA also identified that enforceable guarantees, to ensure that the mitigation measures would be implemented, were necessary to provide a sense of security and control to the community. These guarantees were identified as important in minimizing community impact and reducing community opposition.

BENEFITS OF SIA

The SIAs completed to date for waste management projects indicate that SIA will identify potential social impacts and ways of managing these impacts, assist in resolving conflicts and help to deal with residual effects.

SOME KEY ISSUES IN SIA FOR WASTE MANAGEMENT PLANNING

The following outlines the key issues that have arisen in recent SIA's in waste management that should be anticipated and planned for:

1. Even with state-of-the-art technology and optimum siting, the SIA will identify residual effects with respect to such effects as noise, dust, visual, odours and traffic under occasional adverse conditions due to landfilling. These effects lead to the demand for compensation by local residents and host communities.

2. Social equity issues arise in identification of preferred sites.

3. Perceived effects will be raised by the public; and

4. Host communities and affected residents may have low confidence in design and operations procedures put forward by the proponent to manage social impacts.

SOME FUTURE INITIATIVES IN SIA FOR WASTE MANAGEMENT PLANNING

The following future initiatives respond to the key issues that have reoccurred in recent SIA's:

1. Recognize at the outset the need for intensive SIA with an associated public consultation program.

2. Recognize and plan to accommodate compensation to the affected residents and host community in some form.

3. Recognize and assess social equity issues.

4. Recognize perceived effects.

5. Plan to monitor social impacts during operations and closure including dust, odour, air quality, litter, traffic and visual effects; and

6. Recognize the value of SIA in identification and resolution of issues before the hearing.

Social impact assessment is a relatively new discipline in waste management planning. Consequently, the procedures vary widely by practitioner and the requirements of the expert are not clearly defined. Despite these possible criticisms, the value of SIA in waste management planning is clear given the range of possible effects/social change that come about due to waste management projects. SIA has proven useful in identifying and resolving concerns prior to hearings, in providing recommendations for the management and control of effects, and in dealing with the inevitable residual effects of waste management facilities. We must build on the experiences we have gained to date, anticipate the key social issues that will arise and plan to resolve these issues.

E6

AWARENESS AND PARTICIPATION LEVELS IN HIGH-RISE APARTMENT BUILDING RECYCLING PROGRAMS

Virginia W. Maclaren
Department of Geography
University of Toronto

1.0 INTRODUCTION

This study is the second of a two-stage study on apartment building recycling. While the first stage concentrated on developing a typology of existing waste management practices and source-separation activities in apartment buildings (Maclaren 1988), this stage examines the factors which affect resident awareness and participation levels in existing apartment building recycling programs.

At the time of the study, during the summer of 1988, there were very few apartment building recycling programs in existence in Ontario. This condition is expected to change rapidly in the next few years as municipalities move beyond the now extensively adopted "blue box" curbside program to the more complicated development of recycling in high-rise apartment buildings. Since the success of apartment recycling programs will depend not only on being able to provide facilities for recycling but also on the extent to which residents choose to use these facilities, this report aims to contribute to our understanding of how to achieve the highest participation levels possible.

The report begins by identifying factors which affect awareness and participation in recycling programs. The next section describes the study's research design and response rates for the survey. This is followed by a description of the publicity efforts used in different buildings and the survey of the residents in those buildings. The concluding section summarizes the major findings and discusses the implications of the results for future recycling programs.

2.0 AWARENESS OF THE RECYCLING PROGRAM

Unlike publicity for curbside collection programs, publicity for high-rise apartment recycling programs must be tailored to the individual building. As noted by Maclaren (1988), single family housing has a single type of waste management system (i.e. waste is collected at curbside), while there are many different types of waste management systems possible in apartments buildings, depending on the design of the building. This means that instructions for residents on how to recycle will vary by building type. Another distinguishing characteristic of apartment building recycling programs, in contrast to single family curbside collection programs, is that it is almost impossible to launch a program simultaneously in all buildings in an urban area. Past experience has shown that staged implementation is more likely because of the amount of time needed to approach individual building owners and negotiate an appropriate recycling plan (City of Toronto 1989). Staged implementation and building design differences mean that mass media resources such as

television, radio, and newspapers are not appropriate for publicising the operational characteristics of apartment building recycling programs.

Other methods have to be relied upon to make residents aware of recycling programs in their buildings. These can include: posters, letters, notices, newsletters, or verbal communication from the building superintendent. Residents may also hear about the program by word-of-mouth from their neighbours. Two requirements for effective communication with most of the above publicity methods are literacy (for written communications) and knowledge of the language of communication (for both written and oral communications).

3.0 THE DECISION TO RECYCLE

Once residents become aware of the existence of a recycling program, they can then make the decision to either participate or not participate in the program. Previous research has shown that there are a number of factors which are known to influence this decision. Cook and Berrenberg (1981) suggest that personal satisfaction in behaving consistently with conservation values, and anticipation of social approval or financial gain are factors which actualize intentions to participate in different types of conservation programs, such as recycling. Hertzberg (1983) and Sinclair (1987) have shown that the imposition of mandatory recycling can increase participation levels substantially over those levels achieved in voluntary recycling programs.

Although an individual may be motivated to recycle, previous research has shown that there are also several factors which may inhibit attempts to do so. These include: physical disability; lack of recyclables in the household; storage problems within the apartment unit; and convenience, or the overall effort required to participate. Finally, the effect of both motivating and inhibiting factors have been shown to vary by socio-economic group.

4.0 RESEARCH DESIGN

Since the literature has shown that participation rates in residential recycling programs tend to vary by socio-economic characteristics of the population and the convenience of the program, the survey was designed in such a way as to examine the impact of variation in these two factors. Two types of building tenancy were selected: rental and condominium. Residents of rental units are likely to differ from residents of condominiums in terms of a number of important characteristics, such as income, length of tenancy, and age. The influence of the "social approval" factor may also be stronger in condominiums than in rental units because of the potential for a stronger sense of community in a jointly owned building. Apartment buildings operated by cooperatives or public housing agencies were excluded from the study because of sample size limitations. Senior citizen housing was also excluded.

The convenience of a program was defined in two ways. As noted above, one indicator of convenience is the number of materials that residents are asked to separate. Therefore, buildings with both single material (newspaper only in this case) recycling

programs and multi-material (newspaper, glass, cans) recycling programs were included in the sample. The final factor examined was a second measure of convenience. If residents were asked to set out the sorted materials on their floor, then the program was designated "convenient". In contrast, if residents were requested to carry sorted materials to another floor, then the program was designated "inconvenient".

Given the considerations described above, the following eight high-rise apartment building recycling programs were identified for inclusion in the survey:

1. a condominium with "convenient" newspaper recycling;
2. a condominium with "inconvenient" newspaper recycling;
3. a condominium with "convenient" multi-material recycling;
4. a condominium with "inconvenient" multi-material recycling;
5. a rental building with "convenient" newspaper recycling;
6. a rental building with "inconvenient" newspaper recycling;
7. a rental building with "convenient" multi-material recycling;
8. a rental building with "inconvenient" multi-material recycling.

Unfortunately, not all program[1] types were available in Ontario at the time of the survey (summer, 1988). No condominiums were found to have "convenient" multi-material recycling programs in place. Consequently, this program type was dropped from the study design. An additional problem was that many of the buildings with recycling programs had a fairly small number of units. In order to obtain a reasonable sample size within each program type, it was sometimes necessary to sample from more than a single building. Twelve buildings were ultimately selected, of which three were from Toronto, two from Kitchener, four from Hamilton, two from Guelph, and one from Burlington.

One hundred residents were interviewed from each of the seven program types, using a variety of interview techniques. All interviews were conducted in the evening between the hours of 4:30 PM and 8:30 PM. Apartment units were selected by means of a systematic sample with random starts on each floor. If residents were not home, two callbacks were attempted before selecting another unit in the sample. The overall response rate for the survey was 87%. The high response rate suggests that non-response bias should not be a serious problem.

5.0 METHODS OF PUBLICITY USED IN SURVEYED BUILDINGS

No single publicity method was being used in all of the buildings. Three of the buildings do not provide ongoing publicity about the recycling program. Ongoing publicity is essential for the success of a recycling program since, without it, new residents may not become aware of the existence of the program and old residents may cease participating

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[1]Throughout this report, the term "program type" will be used to refer to buildings in one of the above categories. Although this terminology may be confusing since "program type" also implies different building types (i.e. rental buildings or condominiums), it is meant to simplify the discussion of results.

in the absence of prompts.

Although there is variation in the amount of publicity used in the different buildings, only the rental building with "convenient" newspaper recycling and one of the rental buildings with "inconvenient" newspaper recycling are completely lacking in ongoing publicity. The interviewers noticed that almost all of the posters used to announce the recycling program for the first building had disappeared. In the second building, the only indication of the ongoing nature of the program was the existence of a newspaper recycling bin in the basement.

6.0 RESULTS: RESIDENTS' SURVEY

6.1 Awareness Levels. Residents' awareness levels of recycling programs in their buildings range from a high of 97% in the "inconvenient" multimaterial condominium and the "convenient" newspaper condominium to 54% in the "convenient" newspaper rental program. Application of a chi-squared test to this data indicated that there was a statistically significant relationship between awareness and program type. The outcome of the awareness test appears to be largely attributable to the low awareness levels in the rental building with "convenient" newspaper recycling. This low awareness level may be a consequence of a poor publicity campaign described above for this building.

6.2 Finding Out About the Program. The way in which residents found out about their recycling program varied according to the initial and ongoing publicity methods used in their buildings. However, in buildings lacking an ongoing publicity program, the visibility of the recycling bins and information from neighbours were two of the most important methods of communicating the existence of the program.

6.3 Participation Levels. Net participation levels are the percentage of households participating among those who are aware of the existence of a recycling program in their building. These levels are fairly similar across program types, ranging from 74% to 89%. The rental building with a "convenient" newspaper recycling program exhibits the lowest participation levels, perhaps due, in part, to the lack of an ongoing publicity program in the building. Although the participation rates of sampled residents varied among the different program types, and tended to be lower for the "inconvenient" programs, this variability was not sufficiently strong to be considered statistically significant.

Gross participation levels are simply the participation levels among all households surveyed, regardless of whether they were aware of the program or not. Reflecting primarily the wide variation in awareness levels among the different programs, they range from a high of 90% to a low of 40%. Although no statistically significant relationship was found between net participation and program type, gross participation and program type were found to be related.

6.4 Reasons for Not Participating. The most frequently cited reason for not participating in a recycling program is lack of recyclables within the household (46.9%). The twelve remaining reasons are headed by "too lazy" (11.2%) and "lack of time" (7.1%). Interestingly enough, four of the five buildings in which "lack of recyclables" has been cited by the

highest percentage of respondents (ranging from 43.8% to 86.7%) are rental buildings. A cross-tabulation of this reason against income levels and a difference of means test on household size shows that individuals citing insufficient recyclables as a barrier to participation tend to have lower income levels and smaller households. There is no discernible pattern of responses by program type among the other reasons cited.

6.5 Reasons for Participating. The most frequently cited reason for participating in a recycling program is that the respondent was told to do it by the building's management (24.7%). The next most frequently cited reasons are that it reduces garbage (21.4%), promotes the reuse of materials (19.5%), and conserves resources (17.9%). Four of the 12 reasons cited are related to concern for the environment ("reduces garbage", "conservation", "reduces pollution", and "stops deforestation"); two are related to the economic benefits of recycling ("saves money" and "creates jobs"); and the remainder have no common characteristics.

6.6 Amount of Material Recycled. There is a statistically significant relationship between the amount of newspaper and glass being recycled and the "convenience" of a program. Theory suggests that the amount recycled should be less in buildings with "inconvenient" programs since residents may find it difficult to use the inconvenient recycling facilities on a regular basis. The results show that 97.6% of the respondents in "convenient" programs are recycling 75% or more of their newspaper, while only 88.1% of the respondents in "inconvenient" programs recycle this amount. The percentage of respondents recycling 75% or more of thier glass in "convenient" programs (88.5%) is about 13% higher than the number recycling in "inconvenient" programs. The results for metal recycling are contradictory and not statistically significant. The highest level of metal recycling occurs in an "inconvenient" building; however, the lowest level of metal recycling also occurs in an "inconvenient" building.

6.7 Program Convenience. All participants in the apartment recycling programs were asked to identify one or more aspects of their program which they felt were particularly convenient or inconvenient. Overall, a larger percentage of respondents identified reasons why they felt their recycling program was convenient (43.5%) rather than inconvenient (16.0%). This is, perhaps, an indication of the extent of satisfaction with existing programs. About two-fifths of the participants (40.5%) did not respond to the question.

The two most popular responses, by far, among those participants identifying convenient characteristics were: the recycling bins are in a convenient location (66.2%); and not much effort is required to participate (64.7%). Breaking these two responses down by program type, we find that the proportion of participants from "convenient" programs indicating that the recycling bins are close or convenient is significantly, but not substantively, higher (68.5%) than the proportion in "inconvenient" buildings (60.3%). On the other hand, the proportion of participants from newspaper recycling programs indicating that their program is convenient because not much work is involved (62.8%) is not only not significantly higher than the proportion from buildings with multi-material recycling programs (66.9%), but it is actually lower.

Almost all (82.6%) of the participants identifying characteristics about their program

which they felt to be inconvenient were from "inconvenient" recycling programs. The most frequently cited reason why participants felt their program was inconvenient was one related to the operating characteristics of the recycling program. Just under half (45.9%) of the 98 participants responding to this question felt that there was a problem with storage rooms becoming messy or with bins overflowing. Some participants felt that the program was a personal inconvenience, either because of the amount of work involved in separating materials (17.3%) or because of the problem of spatial constraints on storing goods in an apartment (17.3%). Surprisingly, very few people felt that the location of the recycling bins was inconvenient. In fact, only five of the 81 participants (6.2%) from "inconvenient" programs who identified inconvenient characteristics responded that the bins were too far away.

6.8 Willingness to Source-Separate More Materials. When asked whether they would be willing to recycle more materials, the majority of participants (85.7%) said "yes". This is a positive indication of the degree of enthusiasm that currently participating residents have for recycling. There was no statistically significant relationship between the responses to this question and program type.

6.9 Mandatory Recycling Programs. There was a fairly even split between those who thought recycling should be mandatory for apartment residents (45.1%) and those who thought it should not (46.7%). There was no relationship between attitude towards mandatory recycling and either awareness of or participation in an existing recycling program. On the other hand, the relationship between opinion about mandatory recycling and program type among those currently participating in a program was found to be highly significant. Experience with an existing program appears to affect attitudes towards the imposition of mandatory recycling. The two program types with the highest degree of opposition (57% to 60%) are in condominiums, while the two program types with the lowest degree of opposition (31% to 40%) are in rental buildings. There is no pattern of attitude variability by convenience of the program or by the number of materials being recycled.

Most individuals (18.9%) had no specific reason for favouring mandatory recycling other than the fact that it was a "good idea". Additional reasons cited were related to protection of the environment, efficiency of the program, cost savings, and the feeling that it should be done now rather than later.

Among those objecting to mandatory recycling, most individuals (33.1%), again, had no specific reason other than stating that recycling should remain as a voluntary activity. Other reasons cited included the difficulty of enforcement, problems that the elderly and disabled would have with complying, and the general view that it would be infeasible.

6.10 Program Improvements. At the end of the questionnaire, respondents were asked whether they had any additional comments to make about the recycling program in their building. Almost exactly half of the 291 individuals who had additonal comments expressed their enthusiasm about the program and felt that it was a "good idea". Other comments included: add more materials (17.9%); provide more information (13.7%); provide financial incentives (9.3%); and make the program more convenient (4.8%).

7.0 CONCLUSION

The results of this study stress the importance of effective initial and ongoing publicity for high-rise apartment recycling programs. Even though average participation levels are high, the difference in participation between the buildings with the lowest and highest awareness levels is significant. It is not sufficient simply to provide residents with the opportunity to recycle; residents must be made aware of this opportunity and periodically encouraged to keep participating.

Surprisingly, this study found that the operational characteristics of a program (i.e. convenience, number of materials) do not appear to have a significant effect on participation levels. This result is encouraging since it means that fairly high participation levels can be achieved even when there is a single centrally-located recycling bin in the building and when there is more than a single material included in the program. One qualifier to this conclusion is that, since recycling programs in many of the buildings surveyed had been operating for a fairly short time, the operational characteristics may turn out to have an impact on participation in the long term. A second qualifier is that these conclusions extend only to the materials included in the programs surveyed, namely newspaper, glass, and cans. Although the majority of currently participating households (87.5%) expressed willingness to separate additional materials, the superintendents of many buildings surveyed were pessimistic about the feasibility of adding certain materials, such as food wastes, to their recycling programs.

Finally, the results of this study have shown that participation levels in apartment building recycling programs can achieve levels just as high, or even higher, than those in curbside collection programs. This is a promising conclusion for the expansion of apartment recycling programs across Ontario.

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E7

Estimating the Economic and Financial Impacts of New Federal Environmental Requirements Facing Local Governments in the United States

Brett R. Snyder
Economic Studies Branch
Office of Policy Analysis (PM-221)
U.S. Environmental Protection Agency
401 M Street, S.W.
Washington, D.C. 20460

INTRODUCTION

Municipalities play a major role in supplying environmental services in the United States. Local governments have taken responsibility for providing drinking water, sewage treatment, and waste disposal in a majority of communities. Over the past fifteen to twenty years, most of the mandates found in the federal environmental legislation enacted in the early 1970s have been met. The increase in the number of people served and improvements in the quality of local environmental services have been considerable, as has the investment in public infrastructure to meet these laws.

Recent revisions to the environmental legislation have established a broader and more stringent set of standards to be met by suppliers of environmental services. As a result, many local governments are now faced with having to maintain all or some part of their public services at a higher level of performance. To meet these new standards will require additional investments in capital, and increases in rates charged to customers for environmental services.

The ability of a municipality to meet the requirements of environmental regulations depends not only on which regulations it must meet, but also on its financial health and on how it organizes its environmental services. Geographic, demographic, and political factors all contribute to a municipality's decision to own, operate, and choose the level of environmental services it will provide its citizens. In addition, municipalities that allocate resources to environmental services can effectively reduce expenditures for health care, welfare, and housing.

This study examines what additional investments the new environmental legislation will require local governments to undertake, and the likelihood that they will face difficulties raising the necessary funds through capital markets and revenues from customers. The unique feature of this study is its attempt to estimate the cumulative costs and impacts of meeting a combined set of EPA requirements, and to determine whether they will place a significant burden on the fiscal conditions of local governments, and require them to significantly increase existing charges for environmental services.

STUDY METHODOLOGY AND LIMITATIONS

This study examines the impacts of recent and forthcoming environmental regulations upon user charges and finances in municipalities. The outputs of the study include projections of the cumulative costs to communities of upcoming actions, the proportion of communities expected to face initial difficulties meeting the user charge increases necessary to pay for additional requirements, and the proportion of communities that may have financial difficulties meeting the requirements given their present financial conditions.

Methodology

This study used an EPA model of municipal finances to calculate the effect of adding the estimated aggregate costs of environmental regulations to the current user charges and financial statistics of 270 randomly selected municipalities. As indicators of potential financial difficulties, the study examined several measures of the predicted increases in user fees and municipal debt.

The study estimated the cost and the incidence rate of each environmental regulation for municipalities in each size category to produce estimated "probabilities of occurrence" with relevant associated capital, maintenance, and administrative costs. The probabilities and cost figures were used to determine the weighted average costs of each new requirement, and cumulative totals of weighted average costs for four service categories (i.e., drinking water, wastewater treatment, solid waste, and miscellaneous costs) were used in the analysis. The change in total charges and fees paid by households to meet the new requirements was used as an indicator of the expected severity of the impact to households.

The household burden measure used was the percentage increase in total charges and fees paid relative to current charges and fees. As there is no established limit on what this increase can or should be when addressing the degree of impact to households, the distribution of the cities' percentage increases was analyzed, and several points along the distribution are highlighted.

The study also examined the capability of each city to obtain financing for the additional capital expenditures required for the environmental regulations. Three financial mechanisms were addressed - revenue bonds, general obligation bonds, and bank loans (primarily for smaller communities excluded form bond markets). Revenue bonds are supported by the user charges assessed to customers directly benefiting from the project. General obligation (G.O.) bonds are repaid with revenues raised from property or income taxes. Since revenue bonds rely on customer payments and G.O. bonds rely on the taxing authority of the local government, the revenue bonds are perceived as more risky to investors and, therefore, require a higher rate of return on the amount invested. Revenue bonds can be a more flexible financing instrument than G.O. bonds, since local governments may be constrained by federal and state statutes as to the amount of debt the community can issue, or the amount it can increase tax rates.

The first stage of the financial capability analysis considered whether cities in the sample would have difficulty issuing a revenue bond to cover the costs of meeting additional drinking water or wastewater treatment system requirements. Their ability to meet the requirements was assumed to be contingent upon the condition that the increase in user charges to households necessary to meet additional EPA requirements will not exceed a given level of the household's gross (pre-tax) annual income. Cities that will be required to set user charges at levels that exceed specified ratios of household income (1.0%, 1.25%, and 2.0%) are expected to have potential long-term difficulty issuing a revenue bond to finance the new requirements. These thresholds are derived using information on the distribution of current user charges to households for water services.

The second stage of the financial capability analysis introduces the additional costs for solid waste disposal and miscellaneous requirements, and examines the ability of the city to use city revenues and taxing authority to finance capital requirements. For those cities projected to have long-term difficulty issuing revenue bonds for their drinking water and/or wastewater treatment systems, these costs are included with the solid waste and miscellaneous requirements. Where no long-term difficulties are anticipated for the water and sewer services, only the solid waste and miscellaneous costs are examined against the city's revenue base.

The ability of a city to issue a general obligation bond was assumed to be contingent upon the city's total existing and new environmental debt service obligations relative to two measures: (1) the city's total general revenues, and (2) the city's total market value of assessed taxable property. The first condition measures existing revenue sources, whereas the second condition considers potential revenue sources. A series of threshold values were established using information on the distribution of values for the two measures from the sample of municipalities. The values were used in conjunction with the relevant environmental costs to determine which cities would have potential difficulty issuing general obligation bonds (or for smaller cities, obtaining a bank loan). A city had to exceed the threshold value for both measures before it was assumed to have difficulty using general obligation bonds.

Limitations

Many simplifying assumptions necessary to carry out this study limit its accuracy. The municipal data base consists of a relatively small sample of communities (270), and may not be adequate to form the basis for national estimates. Furthermore, the data base was prepared from fiscal balances for only one year (1986). Because the fiscal conditions of communities continually change with the economy, the data from 1986 may not be representative of the financial conditions that will exist during the 1988-1996 period.

The cost data used in this study were taken from a limited set of EPA regulations. Although about 40 of the 85 regulations considered in the study were identified as having some implications for local government, only 22 were at a stage where cost data were available to be used in the analysis. Several of the omitted new requirements may require significant investments in local government resources (e.g., asbestos in public buildings), or may lead to major changes in current land use patterns (e.g., groundwater protection, nonpoint source guidelines).

In preparing the cost data, it was assumed that small municipalities generally are served by small environmental services systems and large municipalities by large systems. The actual distribution of systems across municipalities may be different, so the costs to households may not be well represented by this method. Furthermore, to reduce the costs of environmental regulations, municipalities may change the way they provide environmental services. Smaller municipalities

may enter into regional services in order to take advantage of scale economies, or they may look to private companies or contractors to provide services, thus freeing themselves of sole responsibility for financing the construction of facilities. They may also find it economical to purchase services from adjacent municipalities or special districts, rather than build new systems to supply the services themselves.

The financial indicators used to estimate households' willingness to pay increased user fees and municipalities' ability to finance capital expenditures are based upon measures currently used in the financial community, but only until local governments make arrangements to raise fees or initiate bond referendum to finance new construction will the preferences of consumers be known. Consumers may be more willing to pay for environmental services than these indicators suggest. On the other hand, some municipalities may have to finance a large number of public works other than those included in this study, and consequently may encounter financial constraints even though they are not predicted to exceed the financial indicators used in the study.

THE IMPACT OF ENVIRONMENTAL REGULATIONS

Environmental Expenses

The estimated increases in environmental expenses for households in municipalities in each of five size categories is presented in Figure 1, both in terms of dollars per household and percent of household income. The largest potential increase in average annual costs per household will occur in communities under 2,500 persons, which will experience an increase of $170 in their annual costs. The households in communities between 2,500 and 250,000 persons will experience a smaller potential increase of $80 to $90 in their annual expenditures for environmental services. Communities over 250,000 persons will also experience large increases in costs for services. The average potential increase in annual costs for the largest communities is $160. The national average increase in annual household costs is $100.

When expressed as a percentage of household income, the greater relative increase in costs to communities under 2,500 persons is more evident. The average increase will require households in the smallest communities spend an additional 0.7% of gross household income on environmental services. Households in communities between 2,500 and 250,000 persons will spend an additional 0.2% to 0.4% of gross household income. Communities over 250,000 will spend an additional 0.5% of gross household income on environmental services.

The individual environmental regulations that account for the largest potential increases in expenses in small communities are the drinking water and sewage treatment requirements. Several of the more costly drinking water regulations will apply more frequently to smaller municipalities. Many larger water supply systems already have introduced treatment systems capable of handling some of these risks. This helps to explain why the overall increases for smaller communities exceed those for the larger communities. Not only do the water regulations lead to relatively large changes in fees in a few cities, but the cumulative costs of the other regulations can add up to sizable increases in user charges and fees for some municipalities.

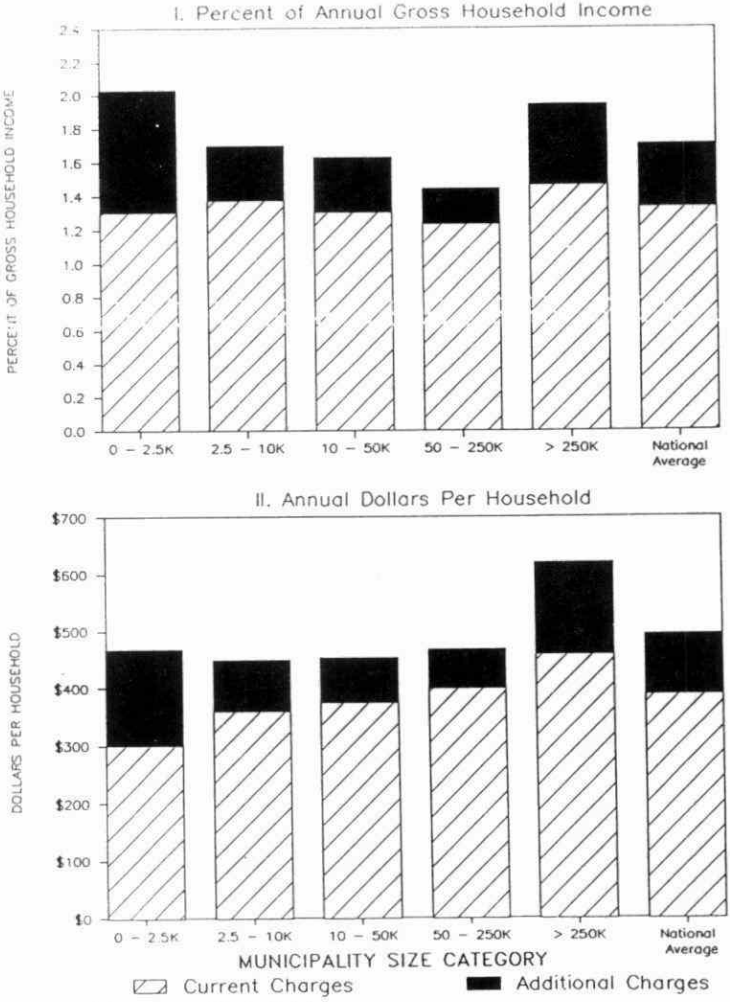
Increases in Household User Charges - Household Burden Measures

When the costs of complying with the environmental regulations are added to existing environmental expenses, the user charges and fees of the vast majority of municipalities will increase. Some municipalities may have to raise user fees considerably above current rates. Table 1 presents information on the number of municipalities that may potentially burden households with requests for large user charge and fee increases. The percentage increases are based on a comparison of current (1986) charges to households for existing environmental services (i.e., drinking water, wastewater treatment, and solid waste disposal) and potential future (1996) charges for environmental services, once all of the additional regulations examined in the analysis are in-place.

Most of the municipalities that would experience the largest overall percentage increases in fees are the smallest municipalities. Of particular interest in Table 1, the user fees of 20% of the municipalities under 2,500 persons may rise over 100% above current levels by 1996. An additional 35% of these sized communities may find their environmental bills increase between 50% and 100%. None of the municipalities above 2,500 persons in the sample are projected to have their household costs rise by over 100%. Although a significant number of larger communities may need to raise household fees between 50% and 100%, most households will not experience large percentage increases in costs of environmental services. Nationally, only 2% of households may have their current environmental service charges and fees rise by more than 100%, and 15% may have to pay between 50% and 100% above their current payments. The Table suggests that many of the households that are expected to experience initial "rate shocks" when confronted with rising user

Figure 1

CURRENT AND POTENTIAL ADDITIONAL AVERAGE ANNUAL HOUSEHOLD COSTS FOR IMPROVED ENVIRONMENTAL SERVICES



Source: Municipal Sector Study Database

Table 1

POTENTIAL CUMULATIVE IMPACT OF ENVIRONMENTAL REGULATIONS:
PERCENT INCREASE IN HOUSEHOLD USER CHARGES

Municipal Size Category	Number of Municipalities	Percent of Municipalities in the Category* Increase as a Percent of Current Charges 0 - 50%	50 - 100%	> 100%
0 - 2,500	26,315 (10%)**	45%	35%	20%
2,500 - 10,000	6,279 (16%)	90	10	0
10,000 - 50,000	2,694 (29%)	80	20	0
50,000 - 250,000	463 (23%)	100	0	0
> 250,000	59 (22%)	80	20	0
Percent of Municipalities		56%	29%	15%
Percent of Population		83%	15%	2%

* This percent increase is calculated as follows:

$$\frac{\text{(Additional Annual Drinking Water + Wastewater + Solid Waste + Miscellaneous Costs)}}{\text{(Current Annual Drinking Water + Wastewater + Solid Waste Costs)}} \times 100\%$$

** Percent of U.S. population living in municipalities and townships within each city size category. According to the 1982 Census of Governments, approximately 85% of U.S. population resides in these government organizations.

fees are in communities having fewer than 2,500 persons.

Capital Financing Indicators

Table 2 presents the percent of cities that may have long-term difficulties raising funds with revenue bonds because of the eventual household rates that must be charged to meet existing and potential EPA requirements. The drinking water and wastewater systems were examined using three different threshold values - 1.0%, 1.25%, and 2.0% of gross household income. As shown in Table 2, if a 1.0% threshold is used, approximately 26% drinking water and wastewater systems in cities under 2,500 persons may have difficulties in revenue bond markets. Raising the threshold to 1.25% of household income reduces this to 12% of systems in cities under 2,500 persons, and raising the threshold up to 2.0% reduces the failure rate down to 2% of systems. Larger city size categories will have less difficulty meeting the additional requirements. For the nation, 21% of drinking water and sewer systems may have difficulty using revenue bonds/loans using the 1.0% threshold. The number drops to 9% of systems when using the 1.25% threshold, and less than 2% using the 2.0% threshold.

Some systems currently have user charges in-place that exceed the lower two income thresholds. The numbers in parentheses in Table 2 show the estimated percentage of systems that exceed the thresholds prior to adding the costs of additional environmental requirements. These systems, as well as systems charging households rates below the thresholds, may need to raise rates further if subject to the additional requirements. Their current conditions may lead to different difficulties in obtaining financing from systems presently below the financial thresholds, and suggest different solutions may be necessary to meet their financial needs. The numbers show that a greater percentage of systems serving communities under 2,500 persons presently exceed the 1.0% and 1.25% thresholds than do systems in larger communities.

The final stage of the financial analysis takes the information from the revenue bond test and combines it with information on solid waste and miscellaneous expenses to determine if the general revenues and taxing authority of the city can be used to finance the remaining environmental services. As shown in Table 3, the cities expected to have the greatest difficulty using city revenues and tax bases to finance additional environmental requirements are in the smaller size categories. The small cities will have greater difficulties meeting the solid waste and miscellaneous EPA requirements, particularly in those instances where the drinking water or wastewater system costs must also rely upon the city's revenue base to raise funds. Between 21% and 30% of cities under 2,500 persons may have difficulty financing the additional EPA requirements.

Small cities that have already committed themselves to large capital projects for environmental or other infrastructure needs, may have to complete these projects prior to investing in new projects. The existing financial condition of the city is more important for the smaller cities, since the large cities appear to have sufficient latitude to finance the additional EPA requirements. Some small cities may be in good financial shape, but the costs of some individual requirements, or the cumulative costs of several requirements that must be met within a short period of time, may strain the financial capability of the community. Therefore, the combination of existing financial conditions and large increases in costs for environmental services in small cities may result in a significant proportion of these cities -- between 21% and 30% -- having financial difficulty meeting the additional EPA requirements.

CONCLUSIONS

The major findings of this study may be summarized as follows:

1. The potential cumulative cost of regulations examined in the study that affect services provided by municipalities may require that the national average household spend an additional $100 per year by 1996.

2. Both municipalities under 2,500 persons and over 250,000 persons will experience the largest average increases in total user charges and fees paid on a per household basis. Some of the more costly regulations address technologies that are in operation at most large cities, but have yet to be adopted by small cities. Also, costs per household for many regulations tend to fall as the population increases, due to economies of scale. These conditions, plus the lower average household income levels in smaller municipalities, will require that households in communities under 2,500 persons pay a greater proportion of their income, on average, for these services than households in larger cities.

Table 2

IMPACT OF ENVIRONMENTAL REGULATIONS ON THE ABILITY OF WATER AND SEWER SYSTEMS TO ISSUE REVENUE BONDS/OBTAIN BANK LOANS IN THE LONG TERM*

Municipal Size Category	Number of Municipalities	Percent of Municipalities that May Be Unable to Issue Revenue Bonds/Obtain Loans in the Long Term: User Charge/ Household Income > 1.0%	User Charge/ Household Income > 1.25%	User Charge/ Household Income > 2.0%
0 - 2,500**	26,315 (10%)***	26% [5%]****	12% [2%]	2% [0%]
2,500 - 10,000	6,279 (16%)	8% [2]	2% [1]	0% [0]
10,000 - 50,000	2,694 (29%)	7% [3]	2% [1]	0% [0]
50,000 - 250,000	463 (23%)	4% [4]	0% [0]	0% [0]
> 250,000	59 (22%)	11% [4]	3% [0]	0% [0]
Percent of Municipalities		21% [4%]	9% [1%]	< 1% [0%]
Percent of Population		9%	3%	< 1%

* Long Term Revenue Bond/Loan Criteria for Drinking Water and Wastewater Services. Percent of cities whose new user charges for either one of the services is greater than the stated threshold value (either 1.0% or 1.25% of gross household income).

** Smaller communities (under 2,500 persons) generally do not issue revenue bonds. Instead they obtain bank loans that are backed by user charges. The criteria used in the revenue bond tests can still be applied to these smaller communities.

*** Percent of U.S. population living in municipalities and townships within each city size category. According to the 1982 Census of Governments, approximately 85% of U.S. population resides in these government organizations.

**** Percent of systems exceeding the threshold prior to incurring potential additional costs of additional requirements (baseline systems failing the criteria).

Table 3

IMPACT OF ENVIRONMENTAL REGULATIONS ON THE ABILITY OF MUNICIPALITIES TO ISSUE GENERAL OBLIGATION BONDS/OBTAIN BANK LOANS

Municipal Size Category	Number of Municipalities	Percent of Municipalities That May Fail to Issue G.O. Bonds/Obtain Loans in Each Size Category* G.O. Bond/Bank Loan Test I	G.O. Bond/Bank Loan Test II
0 - 2,500**	26,315 (10%)***	21% [8%]****	30% [12%]
2,500 - 10,000	6,729 (16%)	4% [3]	9% [9]
10,000 - 50,000	2,694 (29%)	2% [0]	6% [6]
50,000 - 250,000	463 (23%)	0% [0]	0% [0]
> 250,000	59 (22%)	0% [0]	0% [0]
Percent of Municipalities		16% [7%]	24% [11%]
Percent of Population		3%	6%

* Combined G.O. Bond/Loan and Revenue Bond/Loan Thresholds: Capital solid waste and miscellaneous regulatory costs are always examined. The capital costs of drinking water and/or wastewater system requirements are included in calculating required new debt service (total capital costs) if the 1.0% Revenue Bond/Loan Threshold for either system has been exceeded. G.O. Bond/Loan Thresholds - percent of cities exceeding both of the following: (i) Current annual debt service plus new debt service expressed as a percent of current annual city revenues: (Test I: 20%),(Test II: 15%); (ii) Current annual debt service plus new debt service expressed as a percent of the market value of taxable property: (Test I: 0.8%),(Test II: 0.6%). Results using 1.25% and 2.0% threshold are not included because they are not significantly different from results using 1.0% threshold.

** Smaller communities (under 2,500 persons) generally do not issue revenue bonds or general obligation bonds. Instead they obtain bank loans that are backed by user charges. The criteria used in the two bond tests can still be applied to these smaller communities.

*** Percent of U.S. population living in municipalities and townships within each city size category. According to the 1982 Census of Governments, approximately 85% of U.S. population resides in these government organizations.

**** Percent of systems exceeding the threshold prior to incurring potential additional costs of additional requirements (baseline systems failing the criteria).

3. Most municipalities will be able to meet the expected increases in environmental expenses and still remain financially sound. The municipalities most likely to experience difficulty will be the municipalities with populations of 2,500 or less. These communities may have difficulty because of the high cost of some individual regulations, the cumulative costs of recent legislative requirements, and the limited margin for expanding financial obligations in small communities due to existing demands for environmental and other infrastructure services. These difficulties are not limited to small cities, but the results suggest that a much small proportion (between 3% and 7%) of the cities over 2,500 persons will face financial constraints when subject to additional EPA requirements.

Because of the many simplifying assumptions required to carry out this study, care should be taken in interpreting the results. Several of the regulations considered are not yet final, so their costs may change. Other regulations likely to be important for municipalities and households were not included in the cost analysis, and their omission may have resulted in the underestimating of the costs to affected cities. On the other hand, cities may be able to undertake alternative means of meeting environmental objectives that are less costly. The analysis underscores EPA's efforts to seek additional information on the finances and environmental options available for smaller municipalities. Knowing more about small community requirements will assist EPA in better designing and modifying programs capable of dealing with their unique problems.

E8

AN EXPLORATION OF MACROECONOMIC IMPACTS IN THE ENVIRONMENT-ECONOMY LINKAGE

Carl Sonnen, Vice President, Informetrica Limited

Introduction

With the formation of Roundtables on the Environment and Economy at the national and provincial levels, and given the prominence of the persons on these, there is a reasonable chance that major action on the environment will emerge as we move into the 1990s. This could significantly alter the course of future economic activity by removing constraints on growth of the forestry, agriculture and the fisheries, but at the same time, diminish prospects in other sectors. This article summarizes an effort we have made to "add up" initiatives that could be started and completed by the end of the century.

Three, of many, dimensions of the issue are explored. Intervention to reduce the stress of human activity on the environment, or to provide environmental benefits desired by the populace, will use capital, labour and material inputs. In **Case A**, we examine the implications of this, assuming also that private producers attempt to pass these additional costs on in the form of higher prices. Additional costs borne by public institutions are passed on in the form of user fees, or are recovered through taxation. In this case, we assume there are no compensating benefits of such action to the economy.

In **Case B**, we assume that the compensating benefits to the economy are added to the impacts of Case A in the form of cumulating productivity rewards in agriculture and the forestry. In both of the cases, we assume that such additional actions are undertaken by Canada alone.

Case C adds to the assumptions of Case A by assuming that Canadian initiatives are matched worldwide. Thus, as compared to Cases A and B, this impact assumes that Canadian producers directly affected by action are protected from industry loss of competitiveness. Canadian exporters, however, do face the implications of environmental action on the size of the markets to which they sell, and all Canadian consumers face the inflationary implications of worldwide action.

Method and Summary of Assumptions

To measure the effects of actions, we have used standard economic impact techniques. A Base Case projection of the economy is developed under the assumption that "mid-1980" regulations and business practices remain in place over 1989-2005. It is important to note that this case assumes that business and public institutions do record capital and operating expenses to mitigate environmental consequences of their economic activity, and that future capital and production processes may well incorporate more benign environmental design than does existing capital. The case does assume that environmental stress consequent on the assumed future expenditures and behaviour will limit growth of the economy and otherwise have unfavourable economic, human and environmental consequences.

Three alternative projections of the economy are developed representing each of the three cases outlined above. Comparison of each of these alternative projections to the Base Case provides the economic impact

measures.

We have characterized our study as an "exploratory" assessment of issues and impacts in large measure because a rigorous development of the direct action that may, or should, occur cannot be developed. Difficulties of measurement (parts per quadrillion), of translation between disciplines (from a scientific measurement of what needs to be done to the technology and costs of how to do it), of comparison between jurisdictions (which province's legislation and practices is ahead and by how much, and comparisons with states), and indecision on what is going to happen, all make it impossible to develop a rigorous impact statement. Alternatively, we have used "political information", adding up the proposals for action that are currently being suggested across the country, and assuming that all provinces would move to the "best practice" proposals of which we are aware.

Economic Costs of Action - These ball-park estimates include proposals (in some cases, actions) for attacking SOx produced by thermal electric plants and smelters, placing oxygen barriers on mine tailings, Regulation 308 (particulates and air toxics) and MISA-type initiatives (water quality) in Ontario but extended to all of Canada, and renovating or extending water and waste treatment facilities to all municipalities in the country. Our estimates of the total, direct capital and current, expenditures implied by major action are tabulated below.

TOTAL, ALL INDUSTRIES
Capital, Operating and Monitoring Expenses
(in millions of dollars)

	1990	1994	1999	2000	2005
CAPITAL COSTS					
Total ($current)	4678	5412	6143	1450	2195
Cumulated at 1989 Prices	4654	23987	47165	48224	53884
as % of Canadian GDP	0.81	0.74	0.62	0.14	0.15
% impact on Base Case Nonresidential Investment	4.00	3.62	2.93	0.63	0.63
ANNUAL CURRENT EXPENSES ($current)					
Total	1186	6737	15290	16128	21821
Operating	873	5123	12013	12762	17915
Depreciation	303	1603	3263	3346	3879
Ministry Expenditures	10	11	14	21	27
Current Expenses as % of Canadian GDP	0.21	0.92	1.55	1.53	1.48

We assume that the new standards are reached by the end of 1999; to that point, spending includes that necessary to bring the current capital stock up to the new standards, and additional expenditures of future productive investment associated with meeting higher standards. Beyond 2000, continued capital expenditures reflect impacts on new investment made after

that year. We assume that the environmental capital needed for new plant and equipment installed after 1989 will be less expensive than that required to moderate the environmental impacts of existing capital. Costs for adding environmental capital are lower for new investments than for retro-fitting existing capital, and future plant and equipment will likely include environmentally friendly dimensions in its basic design.

A program of this scale would require a cumulated total of an additional $47-48 billion in capital expenditures between now and the end of the Century, and by that time, would be generating additional annual, current expenditures for business and governments of a little more than $11 billion at today's prices. Annual capital expenditures over that period of $4.5-5 billion at today's prices, would be equivalent to between 3 and 4 per cent of investment expenditures otherwise required. For the business sectors directly affected, the additional capital requirements are proportionately much larger, and for governments, this constitutes an increase of 10-12 per cent. Municipalities, especially, would be affected.

Annual current expenditures following from the installation of control and monitoring equipment, or otherwise associated with annual operations of an abatement reduction program, would rise to an amount equivalent to about 1.5 per cent of the Gross Domestic Product we anticipate for the year 2000. The implications for selected industries are much larger, with additional current expenses of rubber and plastics, pulp and paper, iron and steel, non-ferrous smelters, non-metallic minerals and chemicals and the electric utilities' industries equivalent to 3 per cent, or more, of industry value added. For petroleum refining, the share is an order of magnitude larger.

While allocation of the value added that makes up GDP varies from firm to firm, and industry to industry, an average 70 per cent is allocated to payments for labour among goods-producing sectors. Of the remaining amount, an average 13 per cent covers capital consumption allowances, and the balance, 17 per cent, represents a return to shareholders and the crown. Using 4-5 per cent to cover the costs of producing non-marketable outputs like clean air and water takes a substantial bite out of this, implying substantially increased difficulty if new equity is required.

For industries in highly competitive markets, even smaller amounts will pose a difficulty. For regulated industries such as the electric utilities, it will be easier to pass costs on to industrial and household users, though there may be some substitution by other forms of energy.

For provincial and municipal governments, annual current expenditures rise to more than 4 billion dollars at today's prices by the year 2000 to cover expenditures of operating waste and water treatment systems, disposal sites, the hospital system, and the administration of regulations. We have assumed that these governments pay for their costs through increased income and property taxes, and through user fees. By the time all of the new environmental protection is added in 2000, additional, annual taxes and fees amount to $575 per household at today's prices. Since government accounts for about two-fifths of the total action we assume occurs, annual, per-household direct costs would amount to about $1,400 (ex ante) if one assumes that "consumers" ultimately pay for both business and government action.

Economic Benefits of Action - Reduction of environmental stress would produce direct economic benefits. Included should be benefits to productivity in agriculture, the forestry, and fisheries, and associated manufacturing of products produced by these sectors. Tourism may also benefit, though the extent of this would depend on whether action is taken unilaterally, or worldwide.

Reduced damage to capital and human populations will also constitute economic rewards. Accelerated depreciation of structures is a commonly agreed consequence of air pollution. Increased sickness, and death, associated with pollution affects requirements on the health-care system, and limits the size of the labour force, and possibly, through fertility, the size of the population. Arguably, the state of the environment affects the attraction of Canada to immigrants and some foreign investment. Finally, reduction of environmental stress can itself create market-measured outputs. Increased production of sulfur and sulfuric acid are standard by-products of SOx programs.

There is no organized information base that ties programs of the kind we have postulated above back to market-measured, direct economic or population benefits that might result. **Accordingly, we have assumed, for illustrative purposes only, that labour productivity in agriculture and the forestry are improved annually by one per cent.** Thus, productivity is increased over that of the Base Case in each of these two sectors by 12 per cent in 2000, and by 17 per cent by 2005. Likely, these estimates are high, considering, for example, that stress on agriculture of the Prairies from acidification and polluted water is low. On the other hand, our estimates exclude other benefits of the kind noted above.

Unilateral Canadian, or Worldwide, Action? - If Canada proceeds alone, competitive consequences would follow for the industries most directly affected, and perhaps, for the economy as a whole. But this is unlikely, and **Case C assumes there is aggressive, worldwide action.**

We assume there are initial, positive effects on measured economic output in the U.S., and other-OECD, economies followed after the mid-1990s, by a reduction in the size of measured real output of 1.5 per cent by 2005. This is a somewhat smaller impact than is recorded for Canada, but can be rationalized on the more "closed" economic nature of the U.S. economy, and the fact that Canada, by comparison to most others, appears to be currently behind in taking action.

This case represents a scenario in which the Canadian industries directly affected by environmental expenditures lose no significant competitive advantage since their counterparts in the U.S. and elsewhere in the OECD are assumed to face similar additions to their capital and operating costs. On the other hand, real income changes abroad are reduced over the long term, thereby depressing general Canadian exports. Similarly, U.S. and other price levels are increased, and are transmitted into the Canadian economy through import prices.

Economic benefits of worldwide action would reinforce those for Canada of unilateral action. We have no basis for quantifying these, however, and Case C assumes no such offsets. Accordingly, results of this impact can only be compared to those of Case A.

Summary of Economic Impacts

The tabulation below summarizes the economic impacts as measured by a select set of major indicators. As this documents, a major initiative on the environment would likely have initial, positive effects on total, measured output, but long-lasting negative effects. Initial positive effects follow from the dominating impact of additions to demand associated with business and government capital spending required to put monitoring and control equipment into place. Longer lasting negative effects follow from increasing inflationary effects of businesses' attempts to pass higher operating costs on in the form of increased prices, from government application of user fees, and from increased taxes.

Our results suggest that negative impacts on **growth** would emerge within two-three years of a major program's initiation, and that this impact would last through the years that a "program" was being carried out. We do not, however, anticipate that significant negative effects on growth would last past that point (1999 in these results). Further, the long-term, negative impact on the **level** of real activity would likely be modest, with our estimates ranging from 1.5 to 2 per cent.

Direct economic rewards from reduced environmental stress, as is assumed in Case B, would tend to minimize market-measured negative impacts on activity by dampening prices for agricultural and forestry products (in this study) and by reducing unfavourable overall effects on Canada's foreign trade. It will be recalled that there are several other channels through which economic benefits could occur than those we have assumed, while our specific assumptions may be bold. On balance, our reading at this "exploratory" stage is that some negative consequences for general activity are certainly possible. This case suggests an ex post reduction in per-household disposable income in the year 2000 of about $750 measured at today's prices.

Comparison of our Case C and A results suggests that whether one acts unilaterally, or as part of a continental or worldwide program, may be inconsequential to aggregate results. While Canada avoids loss of competitiveness in Case C, any negative effects on real incomes in Canada's foreign markets will shov up as reduced exports. Further, multilateral action will almost certainly yield significantly more inflation for Canada through increased import prices. It should be noted, however, that allowance for direct economic benefits, which were not included in Case C, could easily yield Case B type results.

Although aggregate results are modest, major action on the environment could alter prospects for selected industries by significant amounts. Typically, year-2000 output of metal mines, and in the manufacture of iron and steel, non-ferrous metals, nonmetallic minerals, paper and allied products and chemicals is reduced from Base Case amounts by 5-8 per cent. Given annual growth in these sectors of 2 per cent, or more, over the course of the 1990s, a 5-8 per cent reduction at the end of the century is not sufficient to reduce the size of any of these industries to less than that of today. It could signify, however, notably sloved growth and difficulties for many firms. Our results do suggest that output of petroleum refineries could be reduced substantially over the course of the coming decade. The construction sector, producers of control and monitoring equipment, and "environmental" employees would find substantially enhanced markets during the years in which the program is being phased in.

MAJOR ECONOMIC INDICATORS

	1990	1994	1999	2000	2005
			% Impact		
CASE A					
GNP Value	0.83	1.78	3.59	3.37	3.62
Price	-0.02	1.64	4.60	5.15	5.49
Volume	0.85	0.14	-0.97	-1.69	-1.78
of which:					
Government Expenditure	2.16	3.59	4.59	3.38	3.08
Current	0.38	2.11	3.67	3.70	3.52
Capital	12.01	11.54	9.42	1.69	0.84
Business Investment	2.39	2.03	0.72	-0.74	-0.35
Employment	0.58	0.54	-0.08	-0.56	-0.83
Unemployment Rate (%) (a)	-0.51	-0.55	0.07	0.52	0.95
Wage & Salary/Employee ($C)	0.21	1.24	3.92	4.34	5.16
Consumer Price Index	0.13	1.43	3.88	4.27	4.60
Disposable Income/Capita ($K)	0.18	-0.39	-1.07	-1.27	-0.93
CASE B					
GNP Value	0.85	1.87	3.72	3.52	3.79
Price	-0.02	1.60	4.46	4.99	5.19
Volume	0.87	0.27	-0.71	-1.40	-1.32
of which:					
Government Expenditure	2.16	3.63	4.66	3.46	3.20
Current	0.38	2.11	3.68	3.72	3.54
Capital	12.02	11.77	9.80	2.11	1.43
Business Investment	2.39	2.10	0.85	-0.59	-0.13
Nonresidential	3.09	2.58	1.13	-0.62	0.05
Employment	0.53	0.42	-0.23	-0.72	-1.00
Unemployment Rate (%) (a)	-0.44	-0.38	0.28	0.75	1.21
Wage & Salary/Employee ($C)	0.27	1.42	4.11	4.54	5.30
Consumer Price Index	0.13	1.42	3.82	4.19	4.43
Disposable Income/Capita ($K)	0.21	-0.30	-0.92	-1.11	-0.71
CASE C					
GNP Value	0.82	1.84	4.83	4.89	6.59
Price	-0.06	1.53	5.88	6.79	8.97
Volume	0.87	0.30	-0.99	-1.78	-2.18
of which:					
Government Expenditure	2.16	3.59	4.58	3.37	3.06
Current	0.38	2.10	3.67	3.70	3.53
Capital	12.02	11.57	9.39	1.64	0.63
Business Investment	2.39	2.22	0.42	-1.15	-1.17
Employment	0.60	0.66	-0.14	-0.67	-1.22
Unemployment Rate (%) (a)	-0.52	-0.65	0.08	0.58	1.26
Wage & Salary/Employee ($C)	0.19	1.12	4.93	5.65	8.10
Consumer Price Index	0.09	1.34	5.05	5.75	7.73
Disposable Income/Capita	0.22	-0.35	-1.49	-1.78	-1.83

(a) Level Impact

Concluding Observations

Although the detailed technical inputs needed to produce an authoritative study are not available, we think it safe to conclude that action on the environment could easily lead to very large capital and operating expenses. 1/

Whether one sees our $50 billion investment figure as "big" or not depends on perspective. We have assumed that interest rates are unaffected by action even though there are notable inflationary consequences. If one assumed that the Bank of Canada would react to this with increased interest rates, one could arguably produce a reduction in total output, through increased interest rates and the channels outlined in our analysis, of as much as 3-4 per cent by the year 2000. Still, this would be a modest amount, being equivalent to perhaps one-tenth of the overall output growth that should occur in any event.

At a more personal level, a reduction in household income available for private consumption (or, savings) of $1000 (as a middle-range estimate of ex post effects) by 2000 would represent a notable share of the $4,000-$5,000 increase in disposable income that we anticipate can be generated over the next dozen years when governments are seeking to reduce current debt levels. Other claims for "public goods" (e.g., improved health care, child care, a renovated transportation system) could use up another $1,500, leaving little room for improvement in the disposable income measure of "private" well being. This suggests a more intense competition for resources among claims for new public goods, and between them and household views of private welfare.

For public policy, this poses a challenge to the post-war belief that the country can grow its way out of problems. With average growth of 2 per cent in real, disposable income per household over the past 40 years, the danger that a significant number of people would face a deterioration in their private consumption when there is major restructuring, or a new claim on resources to provide a public good, has been minimized. This will now be more difficult to achieve.

Sectoral details also suggest that major initiatives will bring the "polluter pay" principle under stress. While it may be possible to persuade the "average" household to divert income from purchase of private requirements to public goods, most initiatives will bear directly on a few producing sectors of the economy. In many instances, it will be difficult for them to pass this on to the "average" household, implying concentrated effects on labour and shareholder groups, and on localities and regions. Political realities suggest that devices will be found to avoid forcing the adjustment on these groups. Recent calls for uses of the tax system and development of innovative financial instruments to address environmental concerns suggest

1/ It will be recalled that our $50 billion "program" makes no allowance for new initiatives on CO2 or "agriculture". Press reports in the late Summer of 1989 indicated that investment costs related to CO2 action could range around $75 billion, however. While one cannot add the two figures together, since actions in each "program" area will have effect on the environmental stress of the other, a "round number" of $100 billion in investment costs now seems to be a reasonable starting point for the cost of action. Remember, however, that this still leaves the cost of relieving the "agriculture" problem to be evaluated.

that work on spreading the pain has begun.

Further, since a major program would be large, it is likely that regulations will focus on phasing-in provisions, allowing established firms some prolonged period before new standards must be met, while ensuring that new plants meet the standards as production is begun. This constitutes a form of economic "rent" made available for the existing producer during the interim period, and is a reward for "bad" behaviour.

Finally, accounting for action on CO2 and agriculture, when added to our own view of initiatives, suggests that we need to go beyond choosing between the environment and other public, and private requirements. Action in these areas also provide economic and "utility raising" benefits. Our sizing of the issue suggests that establishing environmental action priorities is also badly needed. This should be difficult. It implies choices among varying environmental interests, and in a pluralist democracy where the electorate often seems to define the environment as a neighborhood question, some of those interests are likely to be ignored.

E9

The Cost of Environmental Protection in the U.S.
Implications for Capital Markets, Local Budgets, and Household Burden

Since the early 1970s, the U.S. Environmental Protection Agency (EPA) has overseen the U.S. national mandate to restore and protect water, land, and air resources. This effort has proven to be a massive undertaking, and the agency has come to rely on its partners -- state and local governments -- to assist in the administration of environmental management programs and expend resources to comply with them. But the expanded programs and tightened controls of the environmental statutes enacted in the 1980s challenge the ability of these partners to finance future environmental needs.

This paper presents estimates of the aggregate public costs of environmental protection; the potential gaps in future funding should current fiscal policies continue; and the implications of such a shortfall for capital markets, local government budgets, and individual households.

WHAT COSTS ARE EXAMINED?

This paper examines expenditures for community drinking water, wastewater treatment, and solid waste management over the period 1981-1987 and projects them to the year 2000. Projections are estimates of the future costs of maintaining today's environmental standards, assuming that future compliance is comparable to current experience. In addition, this paper estimates the costs of new environmental regulations that local governments are expected to bear in the future. These regulations are now on the books in the U.S., but have not yet had a cost effect for local governments. Many more regulations are mandated by U.S. environmental statutes and are now under development. These will undoubtedly increase cost estimates, but they could not be included in this research.

SPENDING WILL HAVE TO INCREASE SIGNIFICANTLY TO MAINTAIN CURRENT PROGRAMS

In 1987, EPA, the states, and local governments spent $40 billion for environmental protection, compared to $31 billion a year a decade earlier.[1]. If recent trends continue, they will need to spend over $55 billion a year by the year 2000, just to maintain 1987 levels of environmental quality (see Figure 1).

This increase is attributable to two factors. First, the cost of providing a base level of environmental protection to a growing population obviously increases as population increases. But beyond the expenditures needed to serve growth, real dollar outlays for environmental protection have outpaced inflation, in response to demands by the American public for cleaner waters, safer drinking water, and more responsible handling of municipal garbage. For example, the average real dollar cost per person of operating the nation's wastewater treatment plants has more than doubled from $15.80 in 1960 to $37.20 in 1984.

THE GAP BETWEEN CURRENT SPENDING AND FUTURE COSTS IS ESTIMATED TO BE NEARLY $21 BILLION A YEAR BY THE YEAR 2000

Spending trends reveal two important cost gaps. The first, about $15.6 billion a year in 2000, is the amount of government spending needed, in addition to 1987 expenditures, to maintain 1987 levels of environmental quality. The second, $5.3 billion a year in 2000, is the amount of local government spending needed to comply with 22 new environmental regulations examined in this paper (see Figure 2).[2]

Together, these gaps represent a difference of nearly $21 billion between what government spent in 1987

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[1]All dollar figures in this paper are expressed as 1988 dollars unless otherwise noted.

[2]A complete listing of these regulations is provided in Appendix A.

Figure 1

Projected EPA, State, and Local Government
Expenditures to Maintain Existing Levels of Environmental
Quality Compared to Their Current Environmental Expenditures

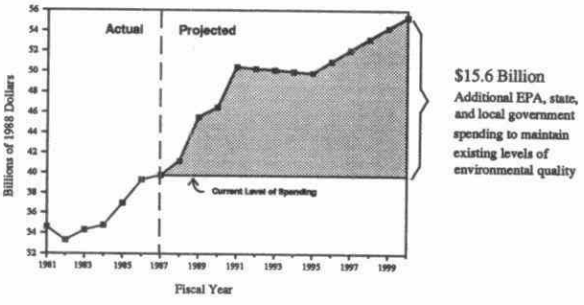
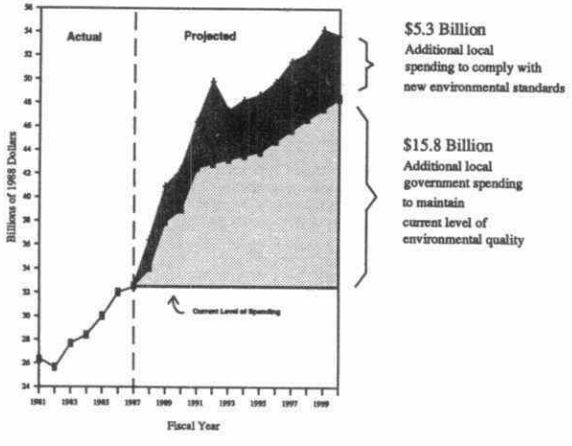

Actual
Projected
Billions of 1988 Dollars
Current Level of Spending
Fiscal Year
$15.6 Billion
Additional EPA, state, and local government spending to maintain existing levels of environmental quality

Figure 2

Projected Local Government Expenditures to Maintain
Current Levels of Environmental Quality Plus Local
Expenditures to Comply With New Environmental Standards


Actual
Projected
Billions of 1988 Dollars
Current Level of Spending
Fiscal Year
$5.3 Billion
Additional local spending to comply with new environmental standards
$15.8 Billion
Additional local government spending to maintain current level of environmental quality

and what we expect them to spend in 2000 for environmental protection. The gap could narrow if we are more efficient in meeting environmental goals. However, these estimates are conservative since they do not include the costs to EPA and the states of many new regulations under development,the costs associated with the future Congressional mandates (such as the forthcoming reauthorization of the Clean Air Act), and the growing number of new state and local environmental mandates.

SPENDING FOR WATER QUALITY WILL INCREASE MORE SLOWLY THAN FOR DRINKING WATER AND SOLID WASTE

With the exception of the air quality program, expenditures to maintain current levels of environmental quality have steadily increased in the 1980s and are expected to continue to do so in the 1990s (see Figure 3). Spending for some programs, however, will increase more than others.

In the 1990s, increases in government spending for water quality are not expected to keep pace with rates of growth in other environmental programs. Between 1987 and 2000, spending for drinking water and solid waste services will increase by 45 percent and 38 percent, respectively. Spending for water quality is expected to increase by only 21 percent (see Figure 4).

THE LOCAL SHARE OF PUBLIC ENVIRONMENTAL SPENDING WILL INCREASE

Local spending is projected to increase significantly by the turn of the century. In 1981, local spending was about $26 billion, or 76 percent of the government share of environmental costs (see Figure 5). By the year 2000, localities will need to spend over $48 billion to maintain 1987 levels of environmental quality and will bear 87 percent of government costs for environmental protection. Adding in the $5.3 billion a year in expenditures to meet new regulations increases the local share to nearly 90 percent.

In contrast, EPA expenditures are expected to decline by about one-third, from $6.3 billion in 1981 to $4.3 billion in 2000. EPA's share of spending on the environment will drop from 13 to 8 percent between 1987 and 2000. This drop is due largely to the phasing-out of EPA grants to build wastewater treatment plants.

Although little is known about future state outlays for environmental programs, trends identified in a recent EPA study suggest that by the year 2000 states will need to spend more than twice the amount spent in 1987 to administer water programs.[3] State administrative costs could triple by 2000 if the air and solid waste programs impose similar demands.

LOCAL DEMANDS FOR CAPITAL ARE PROJECTED TO DOUBLE (1981-2000)

The key issue in examining the impact of environmental spending on capital markets is the ability of local governments to support higher levels of capital formation. We project that annual local demands for capital to maintain current levels of environmental quality could double from about $8 billion in 1981 to over $16 billion in 2000. Additional demands for capital imposed by new regulations will add more than $2 billion a year by 2000 (see Figure 6).

If the gap between current capital formation and future capital requirements for environmental programs were to be financed entirely with new bonds, municipalities would have to issue roughly twice as much environmental debt as they currently do. Compared to the volume of tax-exempt bonds issued to finance water, sewer, and solid waste projects so far in the 1980s -- from $4.5 to $9 billion a year -- this change in volume would not be unusual. In water supply, for example, meeting the capital needs of the 1986 Safe Drinking Water

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[3]State Funding Study, Details of State Needs, Funding, Funding Gap, U.S. Environmental Protection Agency (August 8, 1988). Trends in the State Funding Study were extended from 1995 to 2000 in order to provide consistent data for this report.

Figure 3

Total EPA, State, and Local Government Expenditures to Maintain Current Levels of Environmental Quality, by Media 1981-2000

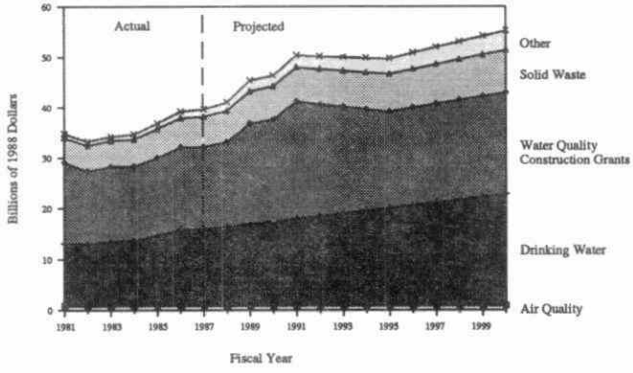
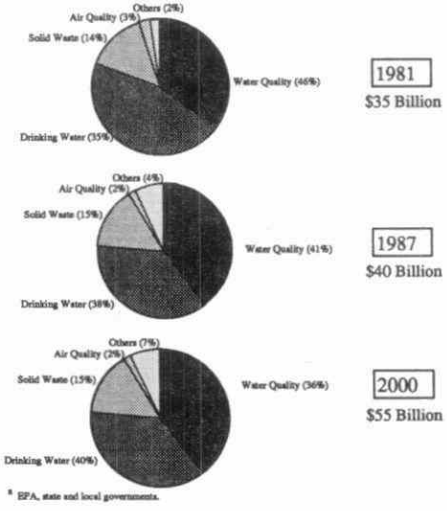


Figure 4

Percentage of Total Public* Expenditures, by Environmental Service, to Maintain Current Levels of Environmental Quality



* EPA, state and local governments.

Figure 5

Proportion of Environmental Outlays (Capital and O & M), by Level of Government, to Maintain Current Levels of Environmental Quality, 1981-2000 (in 1988 Dollars)

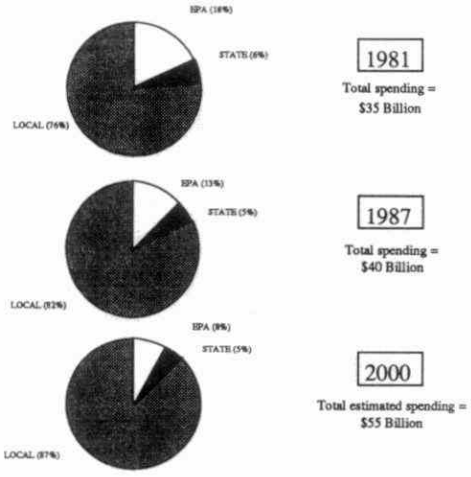
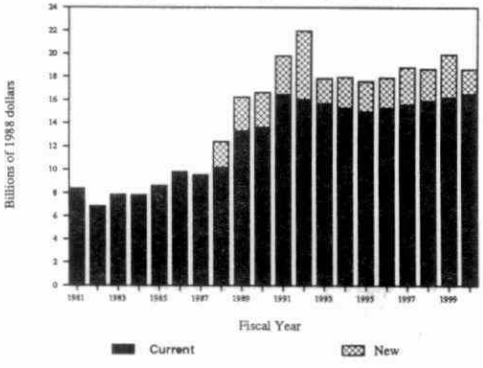


Figure 6

Local Capital Expenditures to Maintain Current Levels of Environmental Quality and Comply with New Regulations, 1981-2000



Act will require an estimated $0.5 billion to $1.0 billion a year in new capital financing over the period 1994 to 2000. This would represent a 25 to 35 percent increase over the current volume of water supply bonds -- fluctuations well within the range in volume for such bonds between 1977 and 1985.

Our analyses indicate that limited ability to pay may make it difficult for small and medium-sized cities to support the levels of debt needed to finance expected environmental facilities.

HOUSEHOLD COSTS IN SMALL COMMUNITIES WILL INCREASE DRAMATICALLY

Costs to households of environmental regulations are measured by increased user charges, increased general taxes, and/or reduced levels of services in other municipal programs. There are also indirect costs, such as when private industries pass their share of environmental costs to households in the form of price increases for goods and services.

The annual real cost of environmental programs for the average household is expected to increase by 54 percent from $419 in 1987 to $647 in 2000 (see Table 1). Over the same period, however, household costs for small cities are expected to increase more dramatically. In cities with fewer than 500 people, they will more than double, from $670 in 1987 to $1,580 in 2000.

The financial impact of environmental costs on households can be examined by measuring costs as a percentage of household income. The results show a significant impact on households in small cities (less than 500 population), for whom expenditures are expected to increase from 2.8 percent to 5.6 percent of household income between 1987 and 2000. On average, impacts are much less for households in all other city size categories, with projected increases of about one-half percentage point to 1.8 percent of household income by the year 2000.

WHERE DO WE GO FROM HERE?

The growing costs of environmental protection suggest the need to reexamine how we make such investments. The large differences between current spending and future costs clearly indicate the need for more innovative ways to finance environmental programs, particularly at the local level.

One way to meet this challenge is to charge more and spend more on environmental services. On the other hand, we could reduce costs by limiting environmental goals. However, increased public support for a cleaner environment suggests that expenditures will increase, not decline.

Finding more efficient ways to supply environmental services is a third option. Apogee has begun working on one way to do this -- forming public-private partnerships to provide environmental services. Greater private involvement can increase public resources available for environmental protection in at least two ways:

- Private equity can free municipal resources for other investments, and
- Even without private financing, properly designed and executed partnerships can provide improved environmental services at the lowest possible cost to the public

We must seek innovative financing strategies, particularly at the local level, to meet the environmental resource challenges facing the U.S. in the 1990s and beyond. This is absolutely necessary if we are to preserve and build on the many important, hard-won environmental gains made during the past two decades.

Table 1. Average Annual Household Payments for Environmental Services for a Sample of 8,032 Cities, Towns, and Townships (1988 dollars)

City Size	Average payments in 1987		Additional payments to maintain **current** environmental and service standards in 2000		Additional payments to comply with **new** environmental and service standards in 2000		Total estimated household payments for environmental protection in 2000
500 or less	$285	+	$501	+	$317	=	$1,103
500-2,500	$254		$205		$67		$526
2,500-10,000	$248		$134		$29		$411
10,000-50,000	$202		$177		$24		$403
50,000-100,000	$136		$124		$24		$284
100,000-250,000	$85		$114		$34		$233
250,000-500,000	$56		$129		$68		$253
500,000 or more	$47		$135		$135		$275
Population Weighted Average	**$180**	+	**$161**	+	**$48**	=	**$389**

Source: Apogee Research, from U.S. Bureau of Census, 1986 Survey of Community Water Systems, and data compiled by the Environmental Law Institute from EPA Regulatory Impact Analyses.

Appendix 1. List of Environmental Regulations included in Our Cost Analysis

Regulation	Status
A. Drinking Water	
Inorganic Compounds (IOCs)	In Development
Synthetic Organic Compounds (SOCs)	In Development
Volatile Organic Compounds (VOCs)	Promulgated
Fluorides	Promulgated
Lead and Copper Corrosion Control	Proposed
Lead and Copper MCL	Proposed
Coliform Monitoring	Proposed
Surface Water Treatment Rule: Filtered	Proposed
Surface Water Treatment Rule: Unfiltered	Proposed
Radionuclides	In Development
Disinfection	In Development
B. Wastewater Treatment	
Secondary Treatment of Municipal Wastewater	Promulgated
Pretreatment Requirements	Promulgated
Sewage Sludge Disposal -- Technical Regulations for Use and Disposal	In Development
Stormwater Management	In Development
C. Solid Waste Disposal	
Municipal Landfill Subtitle D Criteria	Proposed
Municipal Waste Combusters - Air Standards	In Development
Municipal Waste Combusters - Ash Standards	In Development
D. Miscellaneous Regulations	
Underground Storage Tanks - Technical Standards	In Development
Underground Storage Tanks - Financial Standards	Promulgated
Asbestos in Schools Rule	Promulgated
SARA Title III Requirements	Promulgated

Appendix 1. List of Environmental Regulations Applicable to Local Governments But Not Included in the Cost Estimates

Regulations	Status
A. Drinking Water	
Well-head Protection Plan	In Development
Pesticides in Groundwater	In Development
Disinfection By-products	In Development
B. Wastewater Treatment	
National Estuary Program	In Development
Wetlands Protection Program - 404(c) permits	Promulgated
Nonpoint Source Regulations Guidance/Mgmt. Plans	In Development
Section 304(1) - Toxics in Water Bodies	In Development
C. Solid Waste Disposal	
National Contingency Plan - Superfund Program	In Development
Low-Level Radiation Waste Standards	In Development
Toxicity Characteristics of Solid and Hazardous Wastes	In Development
D. Miscellaneous Regulations	
Heavy Duty Diesel Vehicles	Promulgated
Gasoline Marketing	In Development
Diesel Fuel Standards	In Development
Revisions to National Ambient Air Quality Standards (Ozone, Carbon Monoxide, Particulate Matter, Nitrogen Oxides, Sulfur Oxides)	In Development
Asbestos in Public Buildings	May Be Required

E10

PAPER ABSTRACT

ARE ONTARIO'S PROPOSED ENVIRONMENTAL PROTECTION REGULATIONS GOING TO MAKE ITS INDUSTRIES UNCOMPETITIVE?

Eric Cowan*, Apogee Research, Toronto, Canada and **Danielle Hurst**, Hickling Management Consultants, Ottawa, Canada

INTRODUCTION

Governments in the Western developed world are responding to concerns of the electorate by talking about introducing ever-more stringent controls on the toxic pollutants of their industries. While the need for these regulations is clear, there is a concern about their possible effects on the competitiveness of the affected industries. Ontario is considering major changes to its regulations of toxic effluents and emissions of its industries, through the Municipal-Industrial Strategy for Abatement (MISA) and its consideration of changes to its air pollution regulation, Regulation #308. Will the proposed regulations force Ontario's industries to lose market share, move elsewhere, or cancel expansion plans for their Ontario operations?

The approach taken to answering this question in this study, undertaken for the Ontario Ministry of the Environment (MOE), was to compare the current and anticipated industrial toxics regulations of Ontario with the regulations of selected other jurisdictions with which Ontario industry competes. The comparison was done from three perspectives:

- o the extent of toxics regulations in the selected jurisdictions;
- o the extent of enforcement of these regulations; and
- o the financial impacts of these regulations on the affected industries, net of government support and assistance programs.

Ontario was compared to two other Canadian Provinces and 12 selected U.S. States. Nine industry sectors were focused upon as those most likely to bear the heaviest burden under Ontario's proposed regulatory initiatives.

In this paper, we will review the main findings and conclusions arising from this research. We will also discuss briefly the evidence on the effect of the free trade agreement on environmental protection regulations.

SUMMARY OF FINDINGS AND CONCLUSIONS

THE REGULATORY SETTINGS

- o All of the jurisdictions examined are in the midst of proposing major changes to their regulations and enforcement of the toxic effluents and emissions of industries. This complicates the task of comparing the jurisdictions, as all of them are changing simultaneously. It is not always obvious what regulations will result nor when any such regulations will be promulgated.
- o However, all the jurisdictions are moving, and sometimes dramatically so, in the direction of increasing regulation of industry's toxic pollutants. The various agencies involved in developing the regulatory approaches are copying liberally from each and share information freely.

CANADIAN PROVINCES

- All three Provinces have a variety of regulations and licensing processes that impose pollutant controls at specific plants. The emphasis to date has been on the so-called "conventional" pollutants such as pH, suspended solids, and biological oxygen demand (BOD).

- The current regulations result in inconsistent treatment of pollutants, including toxics, among plants in the same sector and across sectors.

- All the Provinces are in the midst of major overhauls of their regulation of air and water toxics. Ontario is much further advanced than the other two Provinces in identifying the specific toxics likely to be regulated and in setting preliminary schedules for regulations.

- Ontario's MISA program has identified 179 parameters, including toxic chemicals, likely to be regulated across the nine priority industry sectors. The proposed amendments to Regulation #308 identify 100 toxic substances that might be regulated.

- Neither Quebec nor Alberta is yet at this advanced stage. However, Quebec has announced publicly a major commitment to environmental protection through its new "Industrial Waste Reduction Program". This program focuses on many of the same sectors that would be regulated under MISA and Regulation #308. While details are still being worked out in government-industry committees, we understand that the Quebec program is being based on both Ontario's approach and the approaches of other jurisdictions that figured in the design of the Ontario model. The Quebec approach will be a technology-based one, as in Ontario, but with greater emphasis on the introduction of clean technologies. If the Quebec government maintains its current momentum it is conceivable that Quebec will introduce controls of toxic pollutants in the same time horizon being considered for MISA and Regulation #308. Quebec's stated target date for introducing toxics regulations is 1992. The specific toxics to be regulated have not yet been identified.

- Alberta is at an earlier stage, and is just developing a process for identifying priority pollutants.

- Quebec is moving towards a "one-stop shopping" approach in its pollution regulation. All regulations and all media will be covered by the "depollution attestation" certificate which will be required. This may simplify the task of compliance on the part of firms.

ONTARIO VS. THE UNITED STATES

- In the U.S., air and water toxics have received different regulatory treatments at the hands of the Environmental Protection Agency (EPA) and are discussed separately.

Water

- For U.S. industries, the EPA has established effluent limits on 126 water-borne toxics (called "priority pollutants") since 1982 for some sectors. These regulations are based on Best Available Technology (BAT-EA). Thus, to the extent that these effluent regulations have been a financial

burden to U.S. industries, the Ontario industries have had a competitive advantage over their U.S. competitors during this period.

- However, in our judgment the U.S. experience has been that the costs to U.S. industry of complying with the EPA's current water-borne toxics regulations have not been significant. The one possible exception to this conclusion is the organic chemicals sector, which may be facing significant capital costs to comply with the regulations.

- Ontario's MISA program is in the pre-regulating stage of monitoring the effluents of the major direct dischargers. The large majority of the EPA's regulated toxics are also on the MISA list. It is highly likely that the EPA's BAT-EA limits will be the minimum levels of control to be specified in the eventual MISA regulations. MISA may impose even more stringent effluent limits, given its stated goal of achieving the "virtual elimination of toxic contaminants in municipal and industrial discharges into waterways."

  Whether or not these future MISA effluent limits will constitute a competitive disadvantage will depend upon the limits set and the costs of achieving them. To date, no estimates have been prepared of the costs to Ontario industries for complying with the eventual MISA regulations.

- U.S. industries are also facing more stringent regulations of their toxic pollutants. Regulations on receiving water quality standards are to be developed during 1989, with enforcement beginning in 1992. These limitations will be in addition to the BAT-EA effluent limits already in force.

- On a per capita basis, Ontario spends three times as much on enforcement as does the U.S. EPA.

Air

- Ontario's proposed amendments to Regulation #308 would cover more chemicals more stringently than comparable programs in the U.S.. To date, the EPA has regulated only seven toxic air substances, far short of the 100 being considered by Ontario. The States have filled this void, proceeding independently. New York has set ambient air quality levels for over 250 toxics, used as guidelines to set permit levels. Massachusetts has ambient standards for over 100 air toxics, also used in the permitting process.

  Some U.S. experts judge that, within two years, the U.S. Federal government will establish a list of air pollutants for which control requirements will have to be set. One piece of legislation in the House of Representatives identifies 187 air toxics to be controlled. Another draft in the Senate directs that 11 specific chemicals are to be controlled within 18 months, with a further 213 chemicals to be controlled within 10 years. Both of these lists cover more chemicals than does Regulation #308.

General

- All of these jurisdictions are operating, to date, on the "polluter pays" principle whereby the industries creating the pollutants are expected to pay the costs of abatement. Thus, there is no competitive advantage in any jurisdiction from this perspective.

- Firms operating in Canada, however, have a significant advantage over their U.S. counterparts in the federal government's accelerated capital cost allowance that the Canadian firms are permitted on their purchases of equipment for purposes of pollution abatement and control. U.S. companies have no such comparable program. The tax-free industrial development bonds available in the U.S. do not compare in impact on the affected companies.

OVERALL CONCLUSIONS

- A detailed comparison of regulations leading to conclusion on competitive advantage is difficult because of the many and complex changes taking place in the toxics regulations of all the jurisdictions and the differences in implementation and enforcement even within a jurisdiction.

- In our view, all the jurisdictions examined will continue to introduce ever-more stringent regulation of industries' toxic pollutants. The call for this increased stringency is being seen by governments to come directly from the electorate.

- The degree of information exchange among the regulating agencies makes it unlikely that the technical toxics regulations themselves will bestow a significant competitive advantage in a jurisdiction. However, the timing of introduction of the regulations could introduce some competitive advantages as each jurisdiction proceeds according to its own time-tables. The detailed effect of this is difficult to judge since governments have traditionally allowed phasing-in periods that can stretch for a decade, especially for special interest groups such as small businesses.

- There will be a tendency for the jurisdictions to "leap-frog" each other, building on the most current technical knowledge, with the level of regulation increasing across all of the jurisdictions.

- Pollution control regulations are, of course, but one of a large number of factors that influence decisions about locating manufacturing and processing plants.

- All of the governments examined claim significant benefits for their industries in exporting pollution control technology to other jurisdictions facing similar regulations. The above results lead to some conclusions about the extent to which these claims are realistic.

E13

Study of the Options for Reduction of Energy-Related Greenhouse Gas Emissions

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Introduction

The World Resources Institute estimates the three leading contributors to the greenhouse effect to be:

. carbon dioxide (CO_2)	49 %
. methane (CH_4)	18 %
. chlorofluorocarbons (CFCs)	14 %

Our research examined ways to reduce energy-related emissions of these gases, with carbon dioxide being the principal focus.

CFCs

CFCs are used as propellants in aerosols, in the manufacture of foams, refrigerants in air conditioners and refrigerators and as cleaning solvents. Halons, compounds related to CFCs, are used in fire extinguishers. Substitutes or alternatives are available, or are expected to become available over the next 5 to 8 years, for most uses of CFCs and halons.

An international agreement, the Montreal Protocol, to limit emissions of CFCs and halons has been signed by 46 countries including Canada. It will reduce CFC consumption to 50 percent of 1986 levels by 1999.

Since the Montreal Protocol was drafted, scientific opinion has concluded that further reductions are needed. As a result, Canada, Ontario and British Columbia have announced their intention to reduce CFC use by 85 percent before 2000 and to eliminate all use as soon as safe substitutes are available.

Eventual elimination of these chemicals appears to be technically and economically achievable. Industry has indicated that it is prepared to cooperate in the achievement of that target.

Methane

Methane emissions are predominantly from natural sources such as wetlands and livestock. The largest energy-related sources are fugitive emissions from the petroleum industry, coal mines, landfills and similar sources.

The estimated annual emissions of fugitive methane and the fraction of those emissions judged to be economically recoverable are as follows:

Source	Estimated Annual Emissions of Methane (millions of m^3)	Fraction Estimated to be Economically Recoverable	Potential Reduction of Fugitive Emissions (1,000 tonnes)
coal mines	500	0.5	180
petroleum industry	2,000	0.1	140
land fills	1,600	0.5	570

Measures to capture and use fugitive methane are technically and economically feasible in many situations. The principal need is for regulations or incentives to encourage collection and use of the methane and to create markets for the gas and/or electricity produced.

Combustion-Related Emissions of CO_2 In Canada

The principal source of carbon dioxide emissions is combustion of fossil fuels. Other sources include feedstock uses of fossil fuels and chemical reactions in the manufacture of cement. This study dealt only with combustion-related emissions of carbon dioxide.

Estimates of current and future emissions of carbon dioxide due to fossil fuel combustion are needed to provide a framework for the analysis of possible abatement options. The following estimates were derived by applying appropriate emissions coefficients to the most recent energy forecast published by the Canadian Department of Energy, Mines and Resources. That forecast is based on the price of a barrel of West Texas crude rising from U.S. $15 in 1988 to U.S. $24 in 2005 (both in 1986 dollars).

The estimated emissions of carbon dioxide due to combustion of fossil fuels are as follows:

	1988	2005	1988 - 2005 Growth
Residential Sector	14	17	15%
Commercial Sector	9	13	53%
Industrial Sector	33	44	35%
Transportation Sector	35	49	40%
Electricity Generation	23	47	104%
TOTAL	114*	171*	50%

* Millions of tonnes of carbon as CO_2 annually.

Currently the transportation and industrial sectors account for about 30 percent of combustion related CO_2 emissions each. Electricity generation is responsible for about 20 percent of the emissions at present. But this sector is forecast to be the most rapidly growing source of emissions. By 2005 electricity generation is forecast to be roughly equivalent to the industrial and transportation sectors as a source of carbon dioxide emissions.

The forecast growth in carbon dioxide emissions continues an historic trend that has been interrupted for most of the past decade. Carbon dioxide emissions in Canada are estimated to have reached a peak in 1979. Since then they have fluctuated in a band down to 10 percent below the peak. This relative stability in carbon dioxide emissions is thought to be due primarily to the sharp increase in energy prices and serious economic recession during the early 1980s. These are probably not the preferred polices for controlling carbon dioxide emissions.

CO_2 Emissions Reduction Target

The June 1988 Toronto conference on "The Changing Atmosphere: Implications for Global Security" recommended a target of 20% reduction from 1988 emissions by 2005. This target appears to be gaining international acceptance. The combustion-related emissions of CO_2 allowed under that target in 2005 are 92 million tonnes of carbon annually.

To meet the target, projected combustion-related emissions of CO_2 must be reduced by 79 million tonnes of carbon per year by 2005. An examination of the projected emissions by sector in 2005 indicates that no single sector exceeds 49 million tonnes. Thus, to reduce CO_2 emissions by 79 million tonnes will require significant reductions in the forecast emissions of several sectors.

Identification of Carbon Dioxide Abatement Measures

Measures with the potential to reduce emissions of greenhouse gases due to combustion of fossil fuels were identified from the available literature. Potential measures were classified into the following categories; measures that:

- conserve energy and so reduce fossil fuel use;
- substitute a less carbonaceous fuel for a more carbonaceous fuel;
- substitute a non-carbon energy source for a carbonaceous fuel;

- remove greenhouse gases from combustion emissions; and
- recycle greenhouse gases.

How Are Carbon Dioxide Abatement Measures Defined?

Each measure is defined in terms of a "typical" installation, such as a house, an automobile, a square metre of commercial floor space, or an industry sector, for which energy performance and financial data are available.

A measure typically involves a specific end use or application and fuel; for example, a building envelope retrofit for homes heated with natural gas. As the example indicates a certain amount of aggregation is needed. A building envelope retrofit may include a variety of specific measures such as ceiling, wall and basement insulation, caulking and weather tightening, storm windows, etc. The "building envelope retrofit" measure used in the analysis reflects a typical mix of these specific measures.

Each measure is documented in terms of its:

- energy performance;
- cost characteristics;
- potential number of installations;
- reduction of greenhouse gas emissions;
- cost-effectiveness in terms of emission reductions; and
- potential for emissions abatement.

CO_2 Emissions Abatement Options

The feasibility of meeting the 20 percent reduction target was assessed by evaluating the technical potential (i.e., 100% penetration of the measure) of selected carbon dioxide abatement options. Abatement options were chosen on the basis of their cost-effectiveness in cutting carbon dioxide emissions (lowest cost per kg of CO_2 emissions avoided).

The abatement options selected on that basis fall into three broad categories:

- improved energy-efficiency of fossil fuel use in the residential, commercial, industrial and transportation sectors. These measures yield carbon dioxide emissions reductions of about 40 million tonnes of carbon per year.

- improved efficiency in the use of electricity through demand side management measures. Adjustments are made for increased cogeneration and use of electrotechnologies. The net impact is to lower carbon dioxide emissions by 19 million tonnes of carbon per year.

- substitution of non-fossil generation for remaining planned and existing fossil fueled generation. This would cut emissions by 29 million tonnes of carbon per year.

The total technical potential for carbon dioxide emission reductions that can be achieved through the selected measures is about 88 million tonnes per year; roughly 10 percent more than the target.

These results reflect a "fantasy world" scenario that assumes full penetration of selected measures and ignores real world barriers. For example, the only sizeable non-fossil generation option available in some regions is nuclear and it is not acceptable to the public in those regions.

As well, the measures are selected solely on the basis of cost-effectiveness in curbing carbon dioxide emissions. Other social objectives and economic impacts are disregarded. Displacing existing fossil-fueled generation would virtually close the coal mining industry, a major source of employment in some areas.

Impacts of Selected Measures on Canadian Electric Utilities

The carbon dioxide abatement measures selected using the cost-effectiveness criterion would have very significant impacts on electric utilities. To wit:

- growth in secondary demand for electricity would fall from 2.54% annually to 0.64% per year over the period to 2005 as a result of the demand side management measures

- all planned and **most existing** fossil fired generating stations would be replaced by non-fossil generation. The additions to hydro and nuclear generation capacity forecast by the Department of Energy, Mines and Resources to 2005 are enough, given the much lower growth in demand, to displace all existing fossil capacity on a national basis.

The impacts on electric utilities under the cost-effectiveness scenario are extreme. This scenario should be treated as only the first step in arriving at a realistic set of CO_2 abatement measures.

Impacts on Other Sectors

Selection of the most cost-effective abatement measures yields reductions in carbon dioxide emissions by the residential, commercial and transportation sectors of 20 to 25%; roughly in line with the overall target. In contrast, emissions from the industrial sector rise by almost 5%.

The major disparity in impacts, then, is between industry and the utilities whose emissions are cut by almost 100%. Electric utilities may be expected to achieve a disproportionate share of the CO_2 emissions abatement target. This does not mean that the financial burden could not be distributed evenly, with direct or indirect transfers from industry to utilities.

Lessons From the Technical Potential Scenario

Recognizing that the technical potential has a "fantasy world" character, it nevertheless yields some helpful insights. Specifically:

- The 20 percent reduction target is very ambitious. The total reduction achieved by 100% penetration of the selected measures exceeds the target only marginally. This means that there is very little scope for sectoral, regional or other exemptions. All sectors and regions will need to make an effective contribution to achievement of the target.

- Major government policy intervention will be needed to achieve the target. Near universal adoption of a broad range of abatement measures across all sectors will not occur in the absence of major policy initiatives.

- In aggregate the selected measures yield a net economic benefit to society on the basis of the energy savings alone. Environmental benefits in the form of reduced climate warming, curtailment of acid rain, lower particulate emissions, etc. increase the benefits further. Costs due to disruption of the electricity generation and coal mining industries could reduce the net benefits somewhat.

E14

COSTS OF ALTERNATE STRATEGIES FOR REDUCING NITROGEN OXIDE AND VOLATILE ORGANIC COMPOUNDS EMISSIONS FROM STATIONARY SOURCES IN ONTARIO

Toby Sanger, David Heeney, and Peter Victor
VHB Research and Consulting, Inc.
Toronto

and

Ruth Reynolds
SENES Consultants Ltd.
Richmond Hill

1 INTRODUCTION

Photochemical oxidants have long been recognized as a cause of vegetative, material, and human health damage. Agricultural crop damage in Canada was first attributed to ozone with the observation of tobacco 'weather fleck' in Southern Ontario in 1955 (MOE 1984). High concentrations of photochemical oxidants have also been observed to cause damage to certain materials, add to atmospheric haziness, and cause health damage to humans. Health warnings to urban dwellers to stay indoors and refrain from strenuous exercise during the hot and hazy days of summer are an unfortunate consequence of elevated ozone levels. Other effects are less sensational but no less important.

Photochemical oxidants are a class of secondary pollutants produced under solar radiation from volatile hydrocarbons and nitrogen oxides. The main oxidants produced by this chain of photochemical reactions include ozone (O_3), peroxyacetyl nitrate (PAN), and nitrogen dioxide (NO_2). While ozone is the principal oxidant produced by this process, it is less toxic than both PAN and NO_2 in some effects.

The time taken to produce these oxidants (from less than one hour to several days) has led to greater consideration of the impact of long range transportation of the emissions associated with this process in order to identify precursor sources and damages. The economic value of increased crop production from ozone reduction was estimated at $15 million (1980$) per year for Ontario alone (MOE 1984).

Efforts to reduce ozone levels have concentrated on the control of precursor compounds: volatile organic compounds (VOCs), comprising both methane and non-methane hydrocarbons, and nitrogen oxides (NO_x).

Damages caused by ozone in Ontario are most acute in Southern Ontario, particularly in the Sarnia region and the metropolitan belt along the Oshawa-Toronto-Hamilton corridor. This area formed the study region for our project. These regions, plus the Nanticoke power generating station along the shore of Lake Erie, are also the source of most of the anthropogenic NO_x and VOCs emissions in the province.

2 MAIN SOURCES OF NO_x AND VOCs

Motor vehicles are by far the largest source of NO_x, responsible for an estimated 65% of 1985 total emissions in this region (ARB 1988) and about the same share for the province of Ontario, as well as for the whole country (Environment Canada 1988). NO_x emissions from motor vehicles are caused by fuel combustion with excess oxygen. Improvements in combustion efficiency and engine modifications can reduce NO_x emissions from motor vehicle engines by up to 70% (VHB 1989).

Motor vehicles are also the largest sources of VOCs in Ontario, responsible for 48% of total VOCs emissions, close to the same share on a national level (Environment Canada 1988). VOCs emissions from motor vehicles result mostly from incomplete combustion and evaporative losses. Evaporative emissions controls, air injection, engine modifications, and oxidation catalysts can reduce VOCs emissions by up to 90% for motor vehicles (VHB 1989).

Emissions from motor vehicles and other transportation sources are necessarily a national problem. Initiatives to further reduce NO_x and VOCs emissions from these sources through stricter emissions standards are currently being undertaken by the Ontario government in concert with the federal government and other provinces.

Fuel combustion by industry, commercial businesses, and the residential sector are the next largest source of NOX, responsible for 29% of the total provincial emissions, 30% of national emissions, and 34% of the emissions in the study region. The electric generating and petroleum refining industries were the source of most of these emissions.

Emissions of VOCs are generated by a wider variety of sources and processes. VOCs emissions from the evaporation of solvents, dry cleaning, gas and fuel marketing, fires, swamps, pigs, and other dispersed sources all account for a large share of the annual VOCs emissions in the province. Process and product changes in solvents and surface coatings, and gas volatility reduction in the fuel marketing network are among the proposals for reducing emissions from these dispersed sources. Industry is also a major direct source of VOCs, particularly the chemical products and the petroleum refining industries. These two industries were each responsible for 6% of the VOCs emissions in the study region. Other industrial sources were responsible for close to another 6%.

Annual emissions from these different sectors are shown in Figure 1 and Figure 2 for both the study region and the province.

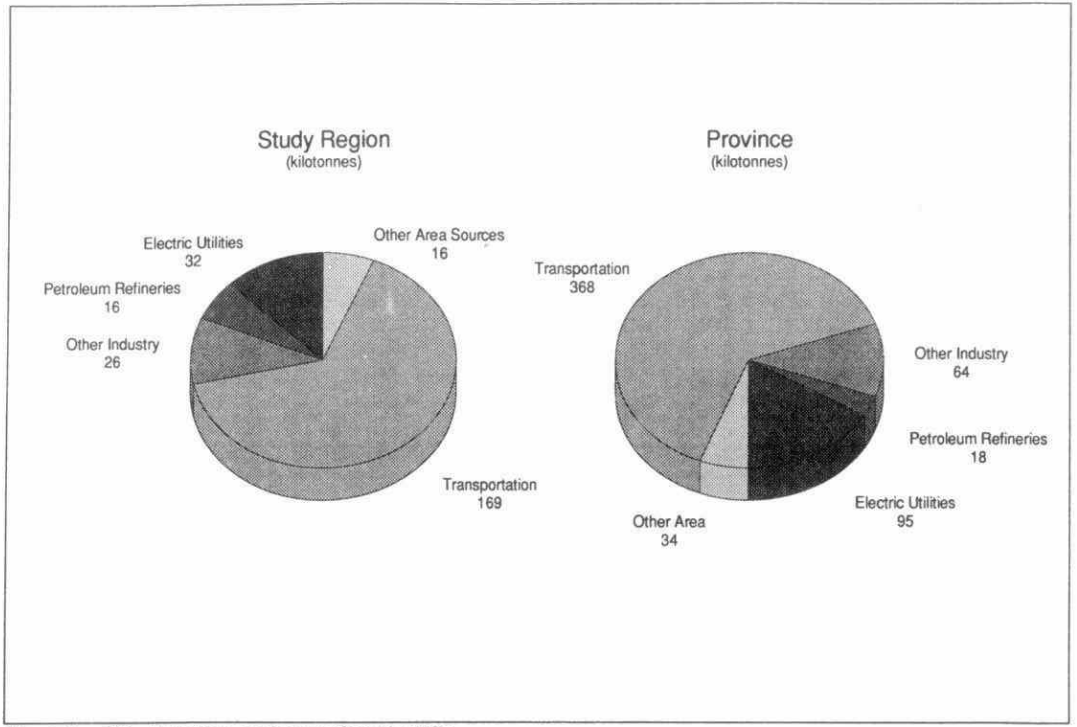

Figure 1 NO_x Emissions by Sector: Ontario 1985

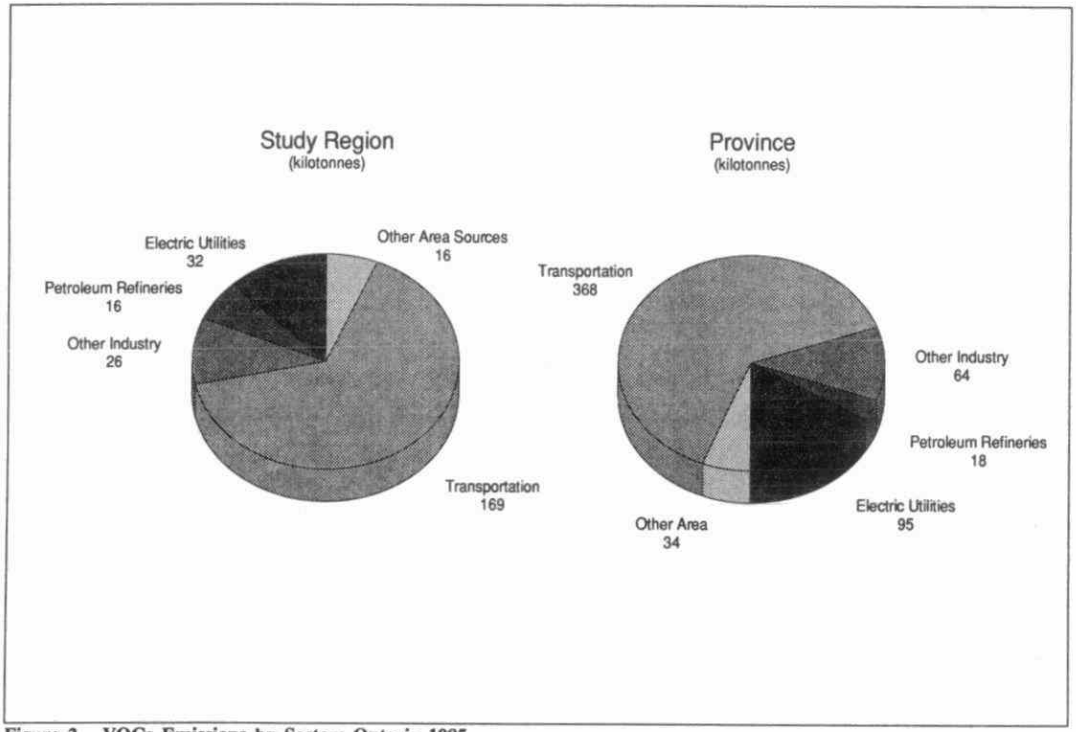

Figure 2 VOCs Emissions by Sector: Ontario 1985

3 STUDY OBJECTIVES

As part of the Ontario Ministry of the Environment's strategy for the control and abatement of oxidants under the Long Range Transportation of Air Pollutants (LRTAP) control program in Ontario, an estimate of the economic costs of alternate abatement strategies was undertaken. This study was to concentrate on emissions from the chemical producers, petroleum refineries, and electric generating stations in the Sarnia and Oshawa-Toronto-Hamilton metropolitan regions.

The specific objectives of our study were to:

- determine the major sources and quantities of NO_x and VOCs emissions in Ontario;
- project future emissions for the specified sectors and regions;
- identify abatement technologies and systems to reduce NO_x and VOCs emissions from these sources;
- estimate capital and operating costs for applicable technologies for each source and use this data to develop abatement cost functions;
- estimate the costs of achieving three abatement strategies.

4 STUDY METHODOLOGY

Data on 460 individual sources of NO_x and VOCs emissions from 41 different industrial establishments was compiled from the *Ontario Emissions Inventory System* database for the three industries in the study area.

Seven different technologies and processes for reducing or controlling VOCs emissions were considered for identified VOCs emission sources: catalytic incineration, thermal incineration, carbon treatment, steam flares, floating roof tanks, piping, and increased maintenance. Six technologies for reducing or controlling NO_x emissions were considered for the sources: low excess air firing, selective catalytic reduction, selective non-catalytic reduction, fuel switching, staged combustion, and low NO_x burners.

While operating costs of pollution control technologies are often related closely to the total loadings of pollutants, capital costs are usually more closely related to other factors, such as flue gas flow rate and burner, equipment, or storage tank size. Detailed capital and operating costs were calculated for the sources where this information was available. Costs for the remaining sources were estimated by extrapolating to emissions emanating from similar industrial processes.

These cost estimates were used to estimate abatement cost functions for each pollutant and by detailed industrial source sector according to three selected scenarios:

- *Lowest Achievable Emission Rate* (LAER) scenario: requiring the use of technology which leads to the lowest level of emissions,
- *Minimum Control Level* on all sources scenario: requiring every emitter to reduce emissions by a target fixed minimum percentage rate (or the lowest achievable rate if such a rate is not achievable),
- *Least Cost* scenario: requiring emitters as a group to implement the least-cost technologies to achieve a specified abatement target.

The three scenarios above are identical when the Minimum Control Level and the Least Cost scenarios are set to maximum or 100% removal *target* levels. That is, the LAER scenario becomes a special case of the other two scenarios.

5 THE EFFECT OF PROGRAM DESIGN

In designing abatement programs, it is important to take into consideration the distribution of both the benefits and the costs of the control measures. The design of the program may have a significant effect on who will benefit from the program, and who must bear the costs of it.

For example, a program requiring all sources to reduce emissions by a minimum fixed percentage will have the effect of distributing the costs widely. However, it is likely that the actual costs of abatement will be heavier on some industries than others and this approach may fail to take into account the different costs already incurred at each end source. The firms most affected by such a strategy are likely to be different than the firms selected by a strategy aimed at achieving the maximum level of abatement at the least cost.

Similarly, there may be significant differences in the distribution of benefits, depending on the abatement strategy pursued. If the industries affected by the least cost abatement program are located in same region, then the effects of the abatement program will be largely restricted to that and downstream regions - and not necessarily where benefits would be maximized.

Where the costs of ensuring distributional equity across sources (regulating a minimum fixed percent reduction at all sources) are considerably higher than a least cost strategy achieving the same reduction, then serious consideration must be given to the issue of trade-offs between distributional equity and economic efficiency.

The distribution of benefits across regions is more difficult to analyse to any degree of accuracy because of the many factors influencing ozone damages: sunlight, prevailing winds patterns, temperature, &c. In many cases, the most that can be expected is to regulate

those sources adjacent to, or upwind of, regions with significant agriculture or population and where excess ozone levels have been measured.

6 RESULTS

Costs were developed using a computer model designed for the study to allow for flexibility in equipment depreciation rates, interest rates, technology removal efficiencies, and for changes in the emission rates of the different sources. Using this computer model, it is also possible to estimate the abatement cost curves for a subsector of sources in a particular region, in a particular industrial subsector, or of a certain size.

The least cost scenario selects control options sequentially in order of lowest incremental cost. These results show the most economically efficient costs of control for each level of reduction as control measures are applied selectively to each source. It is of particular interest for policy-making because it shows the wide range in costs of control for different sources and levels of control. Table 1 presents estimated costs of reducing different levels of NO_x emissions from all the sources in the study region.

Table 1 Nitrogen Oxides Least Cost Scenario

Reduction Level	Incremental Cost (per tonne)	Cumulative Reduction (tonnes)	Cumulative Cost	Average Cumulative Cost (per tonne)
1%	$4	560	$2 088	$4
2%	$20	1 120	$13 400	$12
4%	$56	1 749	$48 500	$28
5%	$501	2 154	$247 945	$115
7%	$2 100	3 196	$1 870 528	$585
22%	$2 100	10 556	$17 600 300	$1 700
26%	$2 800	12 497	$23 019 300	$1 800
38%	$3 400	18 289	$42 616 200	$2 300
40%	$16 100	19 163	$49 996 500	$2 600
42%	$23 300	20 127	$70 857 900	$3 500
49%	$25 900	23 239	$145 003 300	$6 200
50%	$37 600	23 800	$163 017 900	$6 800
54%	$38 200	25 900	$241 119 300	$9 300
55%	$247 800	26 357	$284 101 800	$10 800
55.14%	$6 602 800	26 422	$319 836 000	$12 100

This table and Figure 3 show that incremental costs of control rise rapidly just above 18,500 tonnes reduction - or a global reduction of 38% for the study area - as selective catalytic reduction control technology is adopted by an increasing number of sources.

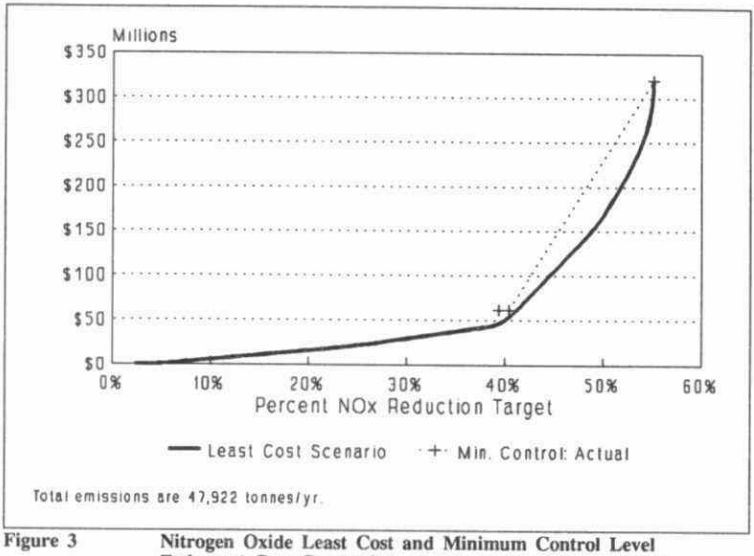

Figure 3 **Nitrogen Oxide Least Cost and Minimum Control Level Estimated Cost Comparison at 10% Interest Rate, 1986$**

Figure 3 provides a comparison of total costs for the least cost and minimum control level scenarios and shows that cost differences at a 40% target level, although relatively small compared to other target levels, can be considerable. The costs of a minimum control strategy at 20% are about three times the costs of a least cost strategy at this level of global reduction. In reality, of course, when many companies install a technology capable of higher removal rates than required under a minimum control level, they would probably not operate the control technology at its maximum removal capacity. Even if they did, the costs of achieving a global reduction of 40% in NO_x under a least cost strategy are over $10 million lower per year than under a minimum control level strategy. For different control levels, or if it is assumed that industries do not operate the control technology efficiently, the cost differential is even greater.

Figure 4 illustrates estimated annual VOCs abatement costs for different reduction levels. The abatement costs start to escalate substantially above 14,000 tonnes reduction - or a 60% global reduction - per year for this group of sources. Applying a minimum control level to all sources would be considerably more expensive than a least cost strategy: $4 million more per year for an 80% reduction and even more for lower target rates.

Estimated annual reductions, costs, and costs per tonne NO_x and VOCs removed under the LAER abatement scenario are shown in Table 2 for different industries.

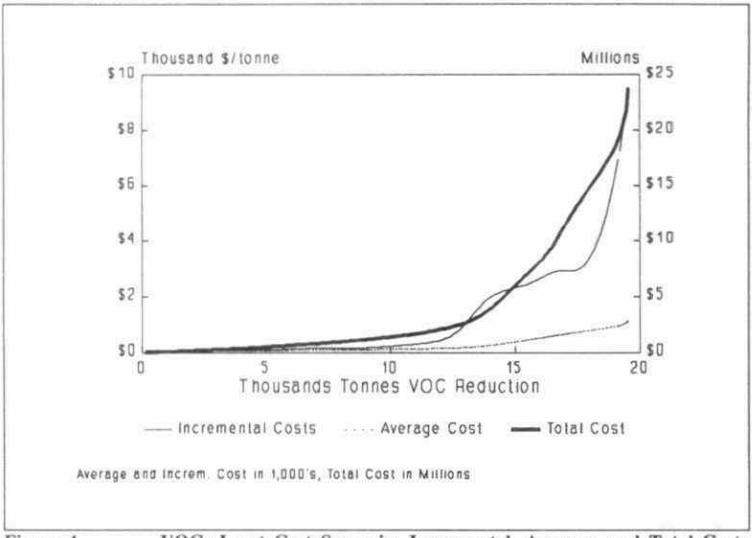

Figure 4 **VOCs Least Cost Scenario: Incremental, Average, and Total Costs At 10% Interest Rate, 1986$**

7 STUDY CONCLUSIONS

The main conclusions of this study were:

1. Large savings in abatement costs - in the order of millions each year - can be achieved by adopting a least cost control strategy instead of a minimum control level strategy. Estimated abatement costs should be matched to estimates of the benefits from pollution abatement from each source to estimate net benefits of controlling each source.

2. Adopting a minimum control level strategy can be justified on two grounds: costs of planning, monitoring, and enforcement can be lower than under a least cost strategy; and an equal minimum control level for all sources on the surface seems fairer than a selective least cost strategy. First, the cost savings estimated in this study from adopting a least cost strategy instead of a minimum control level strategy for most reduction levels appear to be high enough to outweigh additional planning, monitoring, and enforcement costs. Second, sources which can be controlled at relatively low cost per tonne removed are usually either larger emitters or emit high pollutant concentration levels. These can be controlled at a lower cost than other sources because of economies of scale in the first case and because of rising marginal costs of reduction at each source in the second case.

Table 2 LAER NO_x and VOCs Abatement Costs

VOCs Reductions	Annual Reduction (tonnes)	Annual Cost ($'000)	Cost per Tonne removed
Petroleum Refineries	17,277	$18,218	$1,054
Chemical Producers	5,921	$4,146	$700
Total	23,198	$22,364	$964
NO_x Reductions	**Annual Reduction (tonnes)**	**Annual Cost ($'000)**	**Cost per Tonne removed**
Electric Utilities	17,422	$178,836	$10,265
Petroleum Refineries	7,612	$118,552	$15,574
Chemical Producers	1,388	$22,448	$12,173
Total	26,422	$319,836	$12,105

Arguably, it is 'fairer' to force these types of polluters to reduce their emissions before forcing smaller or cleaner sources to do so.

3. The abatement costs estimated in this study are likely to be upper level estimates. If the proper incentives are in place, polluters will probably be able to find lower cost process changes other than those examined in this study which achieve reductions at lower costs. Some of the process changes examined in this report were estimated to result in substantial *fuel savings* for many of the firms because they result in *waste reduction* rather than *waste removal*.

4. Some of the control technologies which were examined in this study can result in some *inter-media transfer* of wastes, rather than complete removal. Inter-media transfers from air pollution control equipment are a more important factor for metals, organic, and particulate emissions. This effect of control technologies should be explicitly considered in further studies of this sort and in designing abatement programs.

5. Little information is available on process changes resulting in waste reduction compared to the information available on generic end-of-pipe control technologies. Waste reduction can be more efficient because cost savings can result and inter-media transfers can also be lower. Better housekeeping methods, more inspection and maintenance, recycling, waste exchanges, and waste audits are first steps on this route. More studies examining actual or potential waste reduction process changes in industry are urgently required.

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E15

THE DEVELOPMENT OF AN ECONOMIC MODEL TO EVALUATE COSTS FOR ALTERNATE STRATEGIES FOR THE MANAGEMENT OF TOXIC HEAVY METAL WASTES

by

B. Fleet, Department of Chemistry, and Institute of Environmental Studies, University of Toronto, and Toxics Recovery Systems International (TRSI), Rexdale, Ontario M9W 5M8, J. Kassirer*, A. Brion ,TRSI and T. Sanger, VHB Research and Consulting, Toronto M5S 2T9.

The present paper aims to examine some of the problems in developing economic models to analyze waste management options or compare the costs of alternate waste management strategies. Some results of a study carried out for the Ontario Ministry of the Environment [1,2] to develop an economic model to evaluate costs for toxic heavy metal waste management strategies are presented.

1. THE ECONOMICS OF WASTE MANAGEMENT

Environmental economics is a complex issue with perspectives at several levels. At the Federal government level there is the search for fiscal policies that will most effectively promote protection of the environment. At the provincial or local government level where there is direct interaction with industry, there is the question of seeking economic incentives to promote waste reduction and cost effective waste management policies as well as possibly generating funding to meet environmental cleanup costs. Finally, the companies and industrial waste generators would need to compare the economics of alternate waste management strategies to aid them in their choice of technology. While most focus is on the latter more practical issue, some discussion of government economic policies and incentives is relevant since it has a direct bearing on industrys' environmental planning.

Most developed countries now seem to be favouring the use of market forces to protect the environment. While the mechanisms being employed in different countries vary and are still being explored, the definite trend is towards offering financial incentives to favour clean industries and "polluter pays" charges that exact a price from those who abuse the environment. While selection and monitoring of these policies is undoubtedly a difficult task, one country at least, West Germany, will now include environmental costs in its national statistics. Over the next five years two sets of figures for gross national product will be compiled. The first will remain the traditional total of goods and services while the second would be adjusted to show the cost of using or abusing the environment. Officials at West Germany's environment ministry

*present address Numetrix Inc., Toronto

indicate that although the task of assigning a monetary value to existing resources and the cost of steps being taken to protect them is daunting, the challenge of assessing the cost of restoration of the environment or compensating those who suffer is far more difficult. Thus, shifting the burden of toxic waste management from nature back to industry, the original generator, is the overall goal of modern environmental legislation, evolving from the "the polluter pays" principle of the mid-60's and the impact of RCRA, the Clean Air and Clean Water Acts and MISA in the USA and Canada, and culminating in the "sustainable development" ethics of the Bruntland report.

The economics of toxic waste management is a complex issue for several reasons. The first is the fact that many waste management costs are difficult to quantify , especially those which relate to societal contributions. Second is the fact that industry itself often has poorly defined data on its own waste management costs, having in the past regarded pollution control as an unfortunate cost of staying in business to be avoided or eliminated wherever possible. In the last decade this situation has changed dramatically. Environmental legislation and public pressure has caused industry to accept environmental management as a major component of its operations. Furthermore, there has been the realization that the costs of traditional methods of waste management such as land disposal or deep well injection have been artificially low. Society is now repaying these subsidies via the enormous remediation costs of "Superfund" and other programs.

Private vs Social Costs

There are two main categories of waste management costs; the "private" costs to industry of running its waste management operations and the "social" costs to government and society in supporting those operations. Private costs mainly cover the capital and operating costs of waste management while "social" costs were mainly confined to the subsidized support costs of land disposal, sewer use and water supplies referred to earlier. However, as we are now only too painfully aware, there are much more serious social costs in the issues of waste site cleanup, public health costs and the environmental impairment costs. These factors might be generally described as "the cost of consumption of environmental quality".

Hard vs Soft Costs

The fact that so many waste management costs are intangible or poorly defined at best, presents a serious problem in any attempt to develop an economic model. Thus the various cost factors might be termed "hard" or "soft" where "hard" costs are those costs which are reasonably well defined such as the capital cost of a waste treatment system, whereas "soft costs" might for example, include some of the hidden labour cost components. A more dramatic example might be the "future risk cost" of a given waste treatment strategy [3].

While most of these intangible or societal costs are not generally of concern to industry in their selection of waste management policies, examples such as Love Canal have shown us that the selection of the lowest cost treatment technology is not necessarily the least expensive. There is a certain "risk cost" element in every waste management decision. Also, as we see the inevitable trend towards elimination of subsidized waste management services such as land disposal, sewer use and industrial water supplies, industry is being forced to turn to the more innovative approaches of waste minimization and recycling [4]. The problem for industry still remains, however, that in the selection of the most effective strategy, future estimates of waste management costs must be considered. Unfortunately, although there are many publications describing the economic benefits of waste reduction few of these contain the hard economic data required by industrial management to carry out major policy decisions.

2. ECONOMIC MODELS

A number of attempts have been made to develop economic models to allow government, industry, environmental legislators, companies or waste generators to analyze the costs of various waste management strategies. These models have been both general [5] and industry or waste-type specific [1,2]. A major problem already referred to, is the uncertainty of many cost elements associated with waste management system operations. Since waste management is often not viewed as a profit centre, capital and operating costs may be buried in general overhead costs. In other cases where waste treatment systems were constructed by the company itself, capital costs were often poorly defined. Operating costs are also often uncertain due to the part time nature of many waste management operations. Thus attempts to develop industry or waste-type specific models are often thwarted by the lack of reliable baseline data. Even case study reports of waste management system economics published in technical journals are usually far from reliable. In many of these so-called studies, basic assumptions are not clearly defined and since they are often prepared by equipment manufacturers themselves, the findings also tend to be over optimistic.

Non-Specific Economic Models; Risk Analysis

Since a new waste treatment system may have a lifetime of ten years or more, any economic analysis of alternative strategies must examine future costs based on probable environmental scenarios. The most valuable work in this area has been carried out by Maclean and colleagues [3,5]. Their approach has been to attempt to analyze the "risk cost" associated with various alternatives. Clearly on-site resource recovery and recycling represents the lowest risk, whereas offsite waste transport and disposal provides the highest risk and possible future damage with its contingent future liability for future waste site cleanup. A full-cost accounting

approach is adopted with a 20-year horizon. In addition, projected regulatory changes (e.g. land disposal, indirect compliance costs such as permitting and record keeping costs and less tangible costs are estimated.

Industry or Waste Specific Models

Turning to industry or waste specific models, the model developed by the authors compare the costs of alternate strategies for management of heavy metal wastes. Although this model is industry and waste-type specific, in principle it could be applied to a range of industries, treatment technologies or waste categories. The main objectives of the model are as follows:

1. To estimate the costs of alternate waste management systems to firms in the metal finishing and printed circuit board industries.

2. To estimate some external costs (primarily through subsidized water rates and environmental impacts - which do not enter into an individual firm's economic calculations), and to estimate the costs of alternate waste management systems from a social perspective.

The model provides detailed output information over a 20-year period for the systems being analyzed. Itemized pre- and post-tax data can also be generated. The model is designed to analyze the costs of alternate waste treatment systems. Although the default comparison is between a "zero discharge" system and a "conventional" sludge precipitation system, any two types of systems can be compared if the user provides capital and annual operating cost information for each.

Costs to Individual Firms

Model inputs for the analysis of costs to the firm include capital costs and a full range of operating costs. Capital cost inputs can be disaggregated to separately account for direct equipment costs, direct installation costs, engineering and design costs, contingency costs, and salvage values for more detailed tax and depreciation calculations.

The range of annual operating costs accounted for include: labour, electricity, water supply, water discharge, chemicals, maintenance, manifesting/paperwork, insurance, storage, and costs of sludge transportation and disposal.

The model allows for different depreciation rates, different loan rates and conditions, variable inflation rates, provision for provincial and federal grants to the firm, and evaluation over different time horizons. A "switch" is provided in the computer program to include the capital and operating costs of a water demineralization system, as most Printed Circuit Board plants (and some metal finishing plants) require de-ionized water for rinsing and reconstituting baths.

Survey data from over 40 metal finishing and printed circuit board manufacturers in Ontario were collected and tabulated as part of the study to provide a basis for the estimates of cost variables for conventional sludge precipitation waste management systems. Published estimates of these costs, and engineering cost estimates provided by equipment manufacturers/suppliers, were also considered. The default set of capital and operating costs were estimated from these data, using linear regression techniques to obtain functions relating these costs to an indicator of the magnitude of waste treatment streams. Capital costs were estimated as a function of GPM water usage whereas most operating costs were estimated as a function of annual water usage.

Social Costs

The main external costs associated with waste disposal by heavy metal generating industries in Canada include: public subsidization of water supply and disposal; environmental, health, and social impacts of sludge disposal; environmental and health impacts of water contamination, and public monitoring costs.

The external costs of land disposal of sludge and public subsidization of municipal water supply and treatment for industry were both estimated and included in the model as defaults as external costs. These values were estimated as averages for Ontario or Canada per tonne of waste disposed at municipal landfills or per thousand gallons water supplied or discharged.

Testing of the Model

Linear regression estimates for the slope parameters for many of the cost variables demonstrated satisfactory coefficients of determination (R^2) at a 95% probability level, although the intercept estimates were generally insignificant. The model proved to be robust. A sensitivity test of the model estimates using estimated standard errors yielded a wide maximum range calculated for these estimates, simulation comparisons demonstrated that the model estimated total and individual costs very close to those reported in published case studies.

3. INDUSTRY CASE STUDIES

The original objective of the project was to apply the model to case studies of toxic metal waste generation by three industries; printed circuit board manufacturing, electroplating/metal finishing and gold milling. Initial results have shown that the application of the model to the first of these categories, the printed circuit board industry, has shown very promising results, whereas the latter two industries still require some revisions and modifications to the basic model and its operation in order to provide some useful data.

The reason for this situation is mainly due to the waste generation patterns in these industries. The printed circuit board industry has a well defined waste profile with the main variations being concentration and volume flow rates of the major pollutant species, copper, chelated coper, tin and lead. The electroplating industry on the other hand has a very complex waste generation pattern. A wide variety of plating and processing operations are carried out and waste stream compositions and other external factors (size, profitability, job vs captive shop, etc) similarly vary widely. The gold milling industry is an even more complex situation. Although they are attempting to address new approaches to their traditional waste treatment problems, there is no clear indication that technological solutions are available that are either technically or economically viable.

Case Study of a Printed Circuit Board Manufacturer

Approach

The model was applied to an Ontario printed circuit board manufacturer, using actual cost data derived from the firm. Again, the question was raised: faced with construction of a new plant or installing a new waste treatment system, how would a zero discharge system compare with a conventional (sludge based) system from an economic point of view? It is worth noting that the more usu al situation is where the plant has an existing conventional waste treatment system and is faced with the prospect of writing off the value of this system prior to investing in a new recovery system.

The case study site is a large captive printed circuit board manufacturing facility located in Southern Ontario. The main features of the site are summarized below:

Printed Circuit Board Case Study Site

Shop Type	Printed Circuit Board Captive Shop
Plated Board Area	current- 4,000 sq.ft./day targeted-5,200 sq.ft. by end of the year
Type of Boards	mainly double sided boards with some multilayer and single-sided boards.
Metals Plated	electrolytic (acid) copper, chelated (electroless) copper and tin/lead
Work Day	two 8-hr shifts plus an additional half shift (4-hours) for the electroplating line.
Daily Water Usage	250,000 US gallons per day (g.p.d.).

Results and Discussion

Figure 1 is an output summary provided by the model. The top section lists the key operating conditions; the middle section summarizes each cost category and the resulting annual costs; the bottom section provides a financial comparison of the two systems before and after tax considerations.

For a printed circuit board firm of this size, the zero-discharge system is clearly a wise investment. It provides an internal rate of return of 32% (after tax) and a payback period of 3 years, even without taking into account future increases in the cost of water (influent water and effluent to sewer) and sludge disposal.

The increased expenses (in $CAN) associated with the zero-discharge system are:

* An additional $813,000 to purchase the system.

* An additional $60,000 yearly for maintenance. This difference is abnormally high due to the fact that the case study firm reported maintenance costs for its current installation that were much lower than the industry average.

* An additional $29,000 per year for electricity, to run the electrorecovery cells.

These were more than compensated for by the following savings in operating expenses:

* Savings of $47,000 per year in labor (including overhead).

* Savings of $162,000 per year in chemicals. This is an unusually high difference, as the case study firm reported chemical costs that were much higher than average. Cost savings normally derive from elimination of the flocculants used in creating sludge.

* Savings of $183,000 per year in water and sewage use costs. The case study had water and sewer use rates that were 91 cents (per thousand gallons in and out) lower than the survey average. A rate increase of 91 cents would bring the savings up by $61,000 to $244,000 per year. Expected increases in this area will make a zero-discharge system even more attractive.

* Savings of $29,000 per year in sludge disposal. This is unusually low, because the case study plant generated less sludge than would be average for a plant using 250,000 gpd of water. Note too, that the plant was paying only $102 per tonne for disposal. In the US, the industry average is $CAN 250-500 per tonne and is rapidly escalating. With the impact of free trade, much higher sludge disposal rates can be expected for Ontario firms in the near future.

Figure 1
Model Output for a PCB Manufacturer
(in $CAN)

Daily Water Use:	250,000 Gals	Gallons per Minute	212
Evaluation Horizon	10 years	Annual Water Use (million)	75
Discount Rate	10.0%	Water & Sew. Cost/1000 gal	$2.71
Corporate Tax Rate	51.0%	Disposal Cost (per tonne)	$102
Interest Rate	7.0%	Inflation Rate	0.0%
% Owner's Equity	100.0%	Grants - Provincial	0
Daily Operation	20 hours	- Federal	0
Working Days/Year	300 days		

Capital Costs	Zero-Sludge	Conventional
Total Installed Cost	2,309	1,496
Annual Capital Cost	329	213
Annual Operating Costs		
Maintenance	92	32
Labour	101	158
Chemicals	67	229
Electricity	34	5
Water/Sewage	20	203
Waste Disposal	0	29
Other	1	5
Total Operating Cost	316	661
Total Annual Cost	645	874
Annual Social Costs	0	0
PreTax Net Present Value	4,250	5,557
AfterTax Net Present val	2,228	2,829

Comparison of Systems	Pretax	After-Tax
Net Present Value	1,306	601
Internal Rate of Return	41.07%	31.62%
Annual Payment	(213)	
Payback Period	3	3

Application of the Model: Case Study of a Metal Finishing Plant

The difficulties in modelling waste management options for this industry were mentioned briefly earlier. The wide variability both of waste streams (types of metals, quantities and waste volumes) and types, size and profitability of plants (small job shops up to large, dedicated captive facilities) make selecting case examples of recommended waste management options very difficult. A typical problem in this industry is lack of hard data on waste treatment system performance and costs. A common example is found where a conventional waste treatment system was installed several years ago and has been modified or expanded by the company's own technical staff. An equally common example is where some early examples of recovery technologies were installed in the plant, did not perform satisfactorily in that they were too complex, required too much maintenance or were affected by other impurities and were simply abandoned. This type of response is very common in this industry.

Work is still in progress on the application of the model to the analysis of waste management costs in the metal finishing industry.

4. CONCLUSIONS AND FUTURE DIRECTIONS

A major problem with the development of any economic model to analyze waste or industry-specific waste management costs will be the site-specific nature of each case. As has already been indicated, some industries have a much more uniform waste generation pattern than others. Selection of optimum waste management strategies depends on many factors [3] including the size, type and profitability of the company, the volumes and compositions of the waste streams, and geographic location of the plant.

The selection of optimum waste management strategies may also depend on the interrelations of legislative, regulatory, political and social factors. For example, centralized waste treatment facilities are well established at various sites in Europe, but in North America and even in newly developing countires like Malaysia, there has been a very strong public opposition to the siting of this type of facility.

Expert Systems

One highly promising approach for the selection and screening of optimum waste management strategies is the use of expert systems [4]. Expert systems are a class of computer-based programs that guide an informed program user through the logic of a problem, at the same time asking questions and performing calculations to solve the problem. The expert system approach in this case would consist of assembling a knowledge base of known waste treatment trains along with their performance and costs. Analysis to identify the optimum treatment process would involve the overlapping of two critical paths, regulatory and technology based.

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